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Studies of unimolecular reactions.

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STUDIES OF UNIMOLECULAR REACTIONS

By

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ABSTRACT

The object of this work was to study the metal-carbon bond strengths of the Group IIB metal-methyl alkyls--mercury, cadmium and zinc.

The thermal decompositions of dimethyl mercury, dimethyl cadmium and dimethyl zinc have been studied in a benzene carrier plug-flow gas system. The overall progress of the decompositions was followed by measuring the amount of methane, ethane, ethylene, propane and toluene formed.

All rate constants depended on the total pressure in the system, until a limit of pressure independence was reached above 10 centimetres total pressure. The high pressure rate constants for mercury dimethyl and cadmium dimethyl were determined above this pressure limit.

The reactions of the radicals formed were studied in relation to the carrier gas used. An activation energy for the abstraction reaction of methyl radicals from benzene was determined at infinite total pressure.

The experimental activation energies for the decomposition of cadmium dimethyl and mercury dimethyl was shown to be equal respectively to $D(CH_3 - Cd\cdots CH_3) = 48.8 \pm 1$ kcal $mole^{-1}$ and $D(CH_3 - Hg\cdots CH_3) = 53.7 \pm 1$ kcal $mole^{-1}$.

The existing theories of unimolecular reactions were reviewed. Comparing the present experimental results with

Slater's theory gave a value of 13 for n', the effective number of oscillators, for both cadmium dimethyl and mercury dimethyl. Correction of previous low pressure flow system activation energies using the relationship $E = E_\infty - \frac{1}{2}n' RT\, g(\theta)$ then gave $D(CH_3 - Cd\cdots CH_3) = 50.1 \pm 1$ kcal mole^{-1} and $D(CH_3 - Hg\cdots CH_3) = 54.0 \pm 1$ kcal mole^{-1}, in substantial agreement with the present experimental values.

For the abstraction reaction of methyl radicals with benzene at infinite pressure, the values $E = 10.5$ kcal mole^{-1} and $\log A/(\text{sec}^{-1}) = 11.1$ were obtained.

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TABLE OF NOMENCLATURE

A ..... Pre-exponential Factor of the Arrhenius Equation

A,B,C .... Moments of Inertia of a Molecule

D ..... Bond Dissociation Energy

E ..... Arrhenius Activation Energy

E_∞ ..... Arrhenius Activation Energy at the High Pressure Limit

$\overline{E}$ ..... Mean Bond Energy

h ..... Planck's Constant

K ..... Transmission Coefficient

k ..... Boltzmann's Constant

k_1, k_2 .... Specific Rate Constants

k_∞ ..... Rate Constant at the High Pressure Limit

m ..... Mass of a Molecule

n ..... Number of Atoms in a Molecule

n' ..... Number of Effective Oscillators in a Molecule

R ..... Gas Constant

R_1 ..... Free Radical Group

T ..... Absolute Temperature

ΔH_f° ..... Standard Heat of Formation at 25°C

ν ..... Vibrational Frequency

θ ..... Parameter Related to the Amplitude Factor

σ ..... Symmetry Number

$R(X)$ ..... Rate of Formation of X

s ..... Number of Normal Vibrational Modes

μ ..... Fractions Related to Amplitude Factors

V ..... Overall Rate of Reaction

CHAPTER I

INTRODUCTION

The present research on the Group IIB methyl metallic alkyls had three overall objectives. The first was to determine a pressure independent activation energy for the unimolecular decomposition of these metallic alkyls and to relate these experimentally determined energies to the metal-carbon bond dissociation energy. Secondly, the reactions of the radicals produced by the decomposition and the carrier gas used were to be studied. Finally, the results thus obtained were to be analyzed with the aim of furthering the basic theory of unimolecular reactions if this were feasible.

The methods that can be used to determine the metal-carbon bond dissociation energies in metallic alkyls are rather limited. The radicals produced in the initial split are too reactive to allow any thermal equilibrium method to be used. The molecules are too complex for the successful application of a spectroscopic method. Electron impact experiments will give only an upper limit of the dissociation energy. The derivation of dissociation energies from photochemical results would require a detailed knowledge of the mechanism by which the molecule absorbs energy. If the

absorption is adiabatic, measurement of the photochemical threshold would place an upper limit on the dissociation energy. Activation energies for the thermal decomposition of metallic alkyls have been determined using both static and flow systems. If the process observed experimentally is a unimolecular decomposition producing two radicals whose energy of activation for recombination is small, the experimental activation energy will be a good approximation to the bond dissociation energy. The complexity of the reactions in static systems is such that unambiguous interpretation of the results is almost impossible.

The interpretation of data from experiments in flow systems has been much more satisfactory. In these investigations (1,2,3,4) nitrogen, carbon dioxide, carbon dioxide with added toluene, and toluene alone were used as carrier gases.

The overall bond dissociation energy, $D(CH_3 - M - CH_3)$ is comprised of the two distinct breaks of the metal-methyl bond, $D_1(CH_3 - M\cdots CH_3)$ and $D_2(CH_3\cdots M)$. These may occur separately or simultaneously. This overall energy may usually be obtained by thermochemical measurements. Kinetic measurement of $D_1(CH_3 - M\cdots CH_3)$ then allows $D_2(CH_3\cdots M)$ to be estimated.

Bond Dissociation Energies by the Kinetic Method

The bond dissociation energy, $D(R_1 - R_2)$, may be defined

as the heat of the reaction

$$R_1R_2 \longrightarrow R_1 + R_2$$

at absolute zero and in the ideal gas state. The recombination of R_1 and R_2 may have a finite activation energy [Figure 1, (a)] or zero activation energy [Figure 1, (b)]. Studies of band spectra indicate that the latter is probably the case when R_1 and R_2 are atoms. The activation energy of the following reactions would also appear to be very small.

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (5,6)$$

$$C_2H_5 + C_2H_5 \longrightarrow C_4H_{10} \qquad (7)$$

$$C_3H_7 + C_3H_7 \longrightarrow C_6H_{14} \qquad (8)$$

$$CF_3 + CF_3 \longrightarrow C_2F_6 \qquad (9)$$

$$C_6H_5CH_2 + Br \longrightarrow C_6H_5CH_2Br \qquad (10)$$

The first four reactions have been studied directly. The activation energy of the fifth reaction has been estimated by an indirect method. Acceptance of the fifth reaction as an example of a reaction with a small activation energy must be rather tentative. Although the evidence is not conclusive it is commonly assumed that if either R_1 or R_2 is a simple radical the energy of activation for the recombination is small.

If there is no potential energy barrier for the recombination of two radicals [Figure 1, (b)], the transition state theory predicts that the unimolecular rate constant is

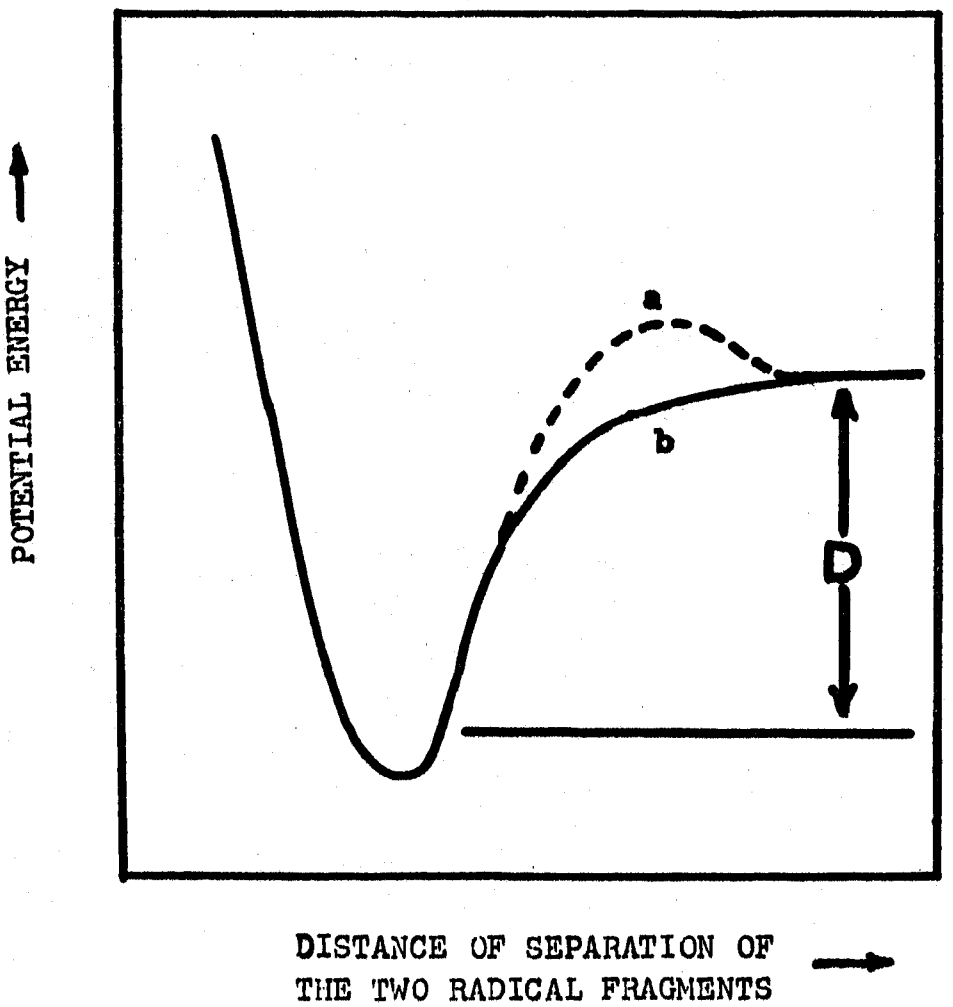


Fig. 1: Potential energy curve for a unimolecular decomposition into two radicals. Curve a represents a finite energy of activation for recombination. Curve b represents a zero energy of activation for recombination.

$$k_1 = K \frac{kT}{h} \frac{\phi^*(T)}{\phi(T)} e^{-D/RT} \qquad [1]$$

The total partition functions, $\phi(T)$ for the normal molecule and $\phi^*(T)$ for the activated complex, may each be separated into translational ($\Lambda(T)$), rotational ($r(T)/\sigma$), and vibrational contributions.

The translational partition function

$$\Lambda(T) = \frac{(2\pi mkT)^{3/2}}{h^3}$$

will be the same for the normal molecule and the activated complex. The rotational partition function will be of the form

$$\frac{r(T)}{\sigma} = \frac{8\pi^2 AkT}{\sigma h^2}$$

for a linear molecule and of the form

$$\frac{r(T)}{\sigma} = \frac{8\pi^2 (2\pi kT)^{3/2} (ABC)^{1/2}}{\sigma h^3}$$

for a non-linear molecule. If each mode of internal vibration behaves as a linear harmonic oscillator equation [1] applied to a non-linear molecule may be written

$$k_1 = K \frac{kT}{h} \frac{\sigma^*}{\sigma} \left(\frac{A^*B^*C^*}{ABC}\right)^{1/2} \frac{\prod^{3n-6} \left(1 - e^{-h\nu/kT}\right)}{\prod^{3n-7} \left(1 - e^{-h\nu/kT}\right)} e^{-D/RT} \qquad [2]$$

If $h\nu \ll kT$ the terms $(1 - e^{-h\nu/kT})$ approach $h\nu/kT$ and

equation [2] becomes

$$k_1 = K \frac{\sigma^*}{\sigma} \left(\frac{A^*B^*C^*}{ABC}\right)^{1/2} \frac{\prod_{3n-6} \nu}{\prod_{3n-7} \nu^*} e^{-D/RT} . \qquad [3]$$

Taking the logs of both sides of [3] and differentiating with respect to temperature gives

$$\frac{d \ln k_1}{dT} = \frac{D}{RT^2} .$$

The Arrhenius activation energy is therefore equal to the bond dissociation energy.

At the other extreme, $h\nu \gg kT$, the terms $(1 - e^{-h\nu/kT})$ approach unity and equation [2] becomes

$$k_1 = K \frac{\sigma^*}{\sigma} \left(\frac{A^*B^*C^*}{ABC}\right)^{1/2} \frac{kT}{h} e^{-D/RT} . \qquad [4]$$

Differentiating the logarithmic form of equation [4] with respect to temperature and rearranging gives

$$\frac{d \ln k_1}{dT} = \frac{D + RT}{RT^2} .$$

Hence, by comparison with the Arrhenius equation, the limits $D \ll E \ll D + RT$ may be placed on the experimental activation energy. It would therefore appear that if the experimental activation energy for a unimolecular decomposition can be accurately determined it should be a reasonable approximation to the dissociation energy of the bond

broken. It should be noted, however, that the above discussion assumes that the experimental activation energy involved is E_∞, the value obtained when the rate constants are determined in the pressure independent region.

Theory of Unimolecular Reactions

The two basic theories of unimolecular reactions, that of N.B.Slater(11,12), and that of Hinshelwood, Kassel, Rice and Ramsperger(13,14,15), hereafter referred to as the H.K.R.R. theory, have recently been discussed by Gill and Laidler(16,17,18).

According to the H.K.R.R. theory, a molecule is considered to be energized if amongst its normal modes there is distributed sufficient energy for the molecule to undergo reaction when this energy eventually finds its way into one particular normal mode of vibration. In the modification due to Kassel, Rice and Ramsperger, the rate with which the required energy passes into the critical normal mode is considered to be a function of the energy that is present in the energized molecule.

In Slater's theory, the basic assumptions are entirely different. The energization of the molecule by collision causes the energy to be distributed statistically between the degrees of freedom and during the subsequent vibrations of the molecule, the energy is not considered to flow between the various modes of vibration.

Slater focuses attention on a critical co-ordinate in the reacting molecule. When this co-ordinate undergoes a sufficient extension, the molecule is considered to undergo reaction. That is, in contrast to the H.K.R.R. assumption of free energy exchange between the normal modes, reaction occurs not when the energy gets into a particular mode, but when the normal mode vibrations come suitably into phase, that is, some critical co-ordinate becomes sufficiently extended.

Hinshelwood's expression for the rate of energization together with Kassel's equation for the rate of breakdown of a critically energized molecule leads to the result that the high pressure first order rate constant is

$$k_{\infty} = k^{\ddagger} e^{-E^{\ddagger}/kT}$$

where $k^{\ddagger}$ is the experimentally determined high pressure frequency factor and $E^{\ddagger}$ is the energy of activation per molecule.

Slater's theory leads to the similar result that

$$k_{\infty} = \nu e^{-E^{\ddagger}/kT}$$

where ν is a specially weighted average of the vibrational frequencies in the molecule.

At low pressures, however, where the kinetics become second order, there are important differences. Related to these differences are divergences between the predicted pressures at which there is a transition from first order

to second order behaviour. This low pressure rate is actually the rate of energization of the molecules and the two different expressions of this rate correspond to the two different definitions of energization.

The definition of energization to which the H.K.R.R. expression applies is that the molecule contains, distributed among its "S" normal modes of vibration, at least the energy $E^{\ddagger}$ required for reaction to occur. The rate of energization to this energy state is, to a good approximation,

$$k_1 = Z \frac{1}{(s-1)!} \left[\frac{E^{\ddagger}}{kT}\right]^{s-1} \cdot e^{-E^{\ddagger}/kT} \qquad [5]$$

where Z is the collision number, S is the number of normal vibrational modes, $E^{\ddagger}$ is the minimum energy required for reaction, k is the Boltzmann constant and T is the absolute temperature. Inherent in this treatment is the assumption that the energy can flow freely between the various modes so that provided the energy $E^{\ddagger}$ is in the molecule, it may, after a sufficient number of vibrations, pass into the one particular normal mode which is involved in the breakdown of the molecule.

According to Kassel's general theory, the first order rate coefficient k^I at any pressure is related to the high pressure rate constant k_∞ by the expression

$$\frac{k^I}{k_\infty} = \frac{1}{(s-1)!}\int_0^\infty \frac{x^{s-1}\, e^{-x}\, dx}{1 + \frac{k^\ddagger}{k_{-1}[A]}\left(\frac{x}{b+x}\right)^{s-1}} \qquad [6]$$

where $x = \frac{E - E^*}{kT}$ and $k^\ddagger$ is a weighted vibrational frequency, k_{-1} is the rate constant for the deactivation process and b is equal to E^*/kT. Numerically, $k^\ddagger = k^*$.

Slater's expression for the second order rate constant is, to a good approximation,

$$k_1 = \nu \left(\frac{E^*}{kT} \cdot 4\pi\right)^{\frac{1}{2}(n-1)} \prod_{k=1}^{n} \mu_k\, e^{-E^*/kT} . \qquad [7]$$

Here the μ_k's are fractions that are related to the so-called amplitude factors, which, in turn are related to the amplitudes of the critical co-ordinate in the various normal modes of vibration. These μ factors can only be obtained by carrying out a detailed vibrational analysis of the molecule. If there is more than one equivalent co-ordinate, equation [7] must be multiplied by the appropriate factor. The sum of the squares of the μ factors is equal to unity so that the maximum possible value that the product $\mu_1 \mu_2 \mu_3 \ldots \mu_n$ can have is $n^{-\frac{1}{2}n}$.

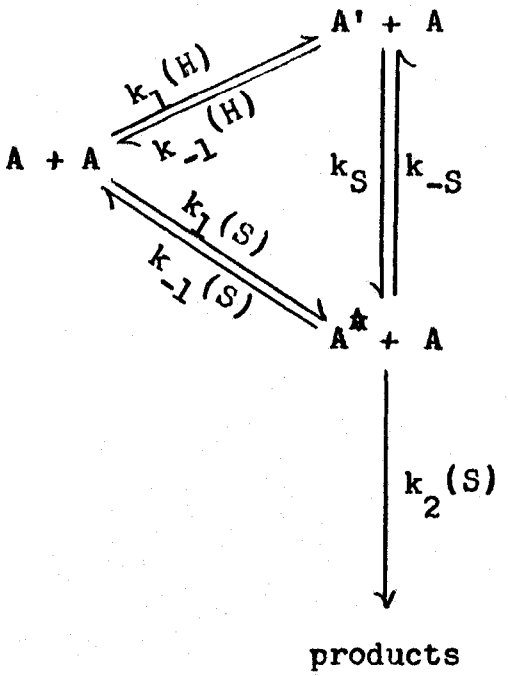
In practice, the product has a much smaller value than this because some of the μ's are usually extremely small, the corresponding normal modes making only a small contribution to the critical co-ordinate.

However, in evaluating the rate constant k_1 it is legitimate to discard any modes of vibration having small values of μ and to employ a corresponding smaller value of n, so as to obtain a maximum rate. Although the distribution of a given amount of energy among a smaller number of degrees of freedom is less probable, it is more likely for the amplitudes to come into phase and give rise to decomposition.

According to Slater, the rate given by equation [7] is always less than that given by equation [5]. This is so because, whereas according to the H.K.R.R. theory a molecule is capable of reaction provided only that it has acquired the energy E^*, this is a necessary but not a sufficient condition for reaction according to Slater's assumptions. For reaction to occur by Slater's mechanisms the energy E^* must be distributed in a particular manner among the normal modes so that when the vibrations come suitably into phase, the molecule reacts.

An extreme case is when one of the μ's is zero, which may occur if the critical co-ordinate is a symmetry co-ordinate. In this case energy is "trapped" in the corresponding normal mode and cannot contribute to the reaction.

Gill and Laidler (16,17,18) suggest as a modification of the unimolecular reaction rate theory a compromise between the assumptions of the Slater and the H.K.R.R. theories. Their reaction scheme is shown below.



In this scheme a distinction has been made between two types of energized molecules, represented by A' and A^*. The A^* molecules are those that are energized in the Slater sense. They not only contain E^* or more of energy, but have it distributed among the normal modes in such a way that, when the vibrations come suitably into phase, there can be sufficient extension of the critical co-ordinate. The A' molecules are those that contain the critical energy E^* but do not have it suitably distributed for reaction to occur without flow of energy.

Slater's condition is a more stringent one than H.K.R.R.'s and the rate constant k_1^S will generally be considerably smaller than k_1^H.

If there can be no energy flow between the modes, the rate constants k_s and k_{-s} are both equal to zero and reaction can therefore occur only by direct energization to A^*. Slater's treatment then applies. If, on the other hand, k_s is not very small, A^* may be formed not only directly but also from A'. At low pressures in fact, most of the A^* may be formed from A' since A' may be formed from A + A much more rapidly than A^* and, at very low pressure practically every A' produced will eventually become an A^*. At intermediate pressures on the other hand, more of the A^* may be produced directly from A + A and Slater's treatment will then apply. On the basis of this mechanism one would therefore expect three regions of kinetic behaviour. The first will be a high pressure region where the kinetics will be first order; here, both A' and A^* will be essentially at equilibrium and the rate of reaction is controlled by the rate of breakdown of A^*. Slater's formula for high pressure rates should apply in this region.

Secondly there is an intermediate pressure region where there is predominantly a direct energization to form A^*. Slater's low pressure formula should apply here.

Then, there is a low pressure region where A^* will be formed predominantly from A' and the H.K.R.R. formula will apply.

Application of the steady state method to the above reaction scheme gives, for the overall rate of reaction,

$$V = \frac{k_2^{S}[A]^2 \left\{k_1^{(S)} k_{-1}^{H}[A] + k_S(k_1^{(S)} + k_1^{H})\right\}}{k_{-1}^{(H)}(k_{-1}^{(S)}[A]+k_2^{(S)})[A] + (k_S k_{-1}^{(S)} + k_{-S}k_{-1}^{H}[A] + k_S k_2^{(S)})} \quad [i]$$

If k_S and k_{-S} are small, equation [i] reduces to

$$V = \frac{k_2^{(S)} k_1^{(S)} [A]^2}{k_{-1}^{(S)} [A] + k_2^{S}}$$

and Slater's treatment applies.

At high pressure under all conditions, [i] reduces to

$$V = \frac{k_2^{(S)} k_1^{(S)}}{k_{-1}^{(S)}} [A]$$

so that Slater's expression for the high pressure rate will always apply, even if k_S is large.

At very low pressures [i] reduces to

$$V = (k_1^{(S)} + k_1^{(H)}) [A]^2$$

which, since k_1 is probably always much greater than $k_1^{(S)}$ becomes

$$V = k_1^{(H)} [A]^2 .$$

At very low pressures, the rates should therefore be given by the H.K.R.R. formula for the rate of energization.

A number of tests have been made by Gill and Laidler

(16,17,18) on experimental molecules using the preceeding scheme with quite favourable agreement between experiment and theoretical prediction.

Pressure Dependence of the Experimental Activation Energy

It has been postulated by Slater (12) that if the unimolecular rate constant is measured in a pressure dependent region the experimental activation energy, E, is related to the experimental activation energy at infinite pressure, E_∞ by the equation

$$E = E_\infty - \tfrac{1}{2} n' RT\, g(\theta)$$

where n' is the number of effective oscillators in the molecule and $g(\theta)$ represents the fractional drop of E from the high value (E_∞) toward the low value ($E_\infty - \tfrac{1}{2} n' RT$). It was previously shown that the experimental activation energy for a unimolecular dissociation lies within the limits of $D \leqslant E \leqslant D + RT$. The assumption that $E = E_\infty$ is inherent in the derivation of this result. Therefore, if the experimental activation energy has been determined in a pressure dependent region the magnitude of $E_\infty - E$ must be determined in order to estimate the bond dissociation energy.

The calculation of k/k_∞ and hence of $g(\theta)$ requires a complete vibrational analysis of the molecule in question. This is usually not available. An approximate value of k/k_∞ may be obtained by comparing the shape of the curve

log k versus log p obtained experimentally with the slope of the log k/k_{∞} versus log p curve for some similar molecule. Values of k/k_{∞} as a function of the pressure dependent parameter θ have been tabulated by Slater (12) for various values of n' from one to thirteen. The necessary data for the conversion of θ to the corresponding pressures are also given.

Using these values, a suitable correction to the experimentally determined activation energy in a pressure dependent region can be made and a value for E_{∞}, the activation energy at infinite pressure, can be determined.

Toluene Carrier Technique

The experimental activation energy may be determined by measuring the unimolecular rate constant at various temperatures. Careful experimentation may lead to a high degree of precision, but unless competing surface and side reactions are absent the rate constant determined will not be that of the unimolecular decomposition. Simple flow systems have often been used in an attempt to reduce side reactions by working at very low concentrations. Szwarc (19) made a study of toluene by a modification of this method in which toluene acted as both reactant and carrier gas. He found that if only a small percentage of toluene decomposed, the reaction could be represented by a simple mechanistic scheme. However, the usefulness of this method is limited

to compounds that satisfy two conditions. First, the radicals formed should be considerably resonance stabilized so that the compounds will lose atoms or small radical groups fairly readily. Second, the radicals produced should not readily undergo further decomposition.

For the study of radical elimination reactions which do not readily satisfy the above requirements, Szwarc (20) developed the toluene carrier technique. The technique is based on the stability of the benzyl radical and the ease of the hydrogen abstraction reaction between many radicals and toluene.

$$C_6H_5CH_3 + R = C_6H_5CH_2 + RH$$

The benzyl radicals produced do not react in the hot zone under the experimental condition used and eventually dimerize outside the main reaction zone. This method can only be considered for reactions where the bond is weaker than the C – H bond in toluene, so that the temperature at which the reaction is allowed to take place is below that at which toluene itself decomposes. However, for higher temperature work, in the region of 800°C, Price (21) has studied the decomposition of toluene, so that suitable corrections can be made for the decomposition of the carrier itself.

However, above temperatures of 875° to 900°C, too many permanent gases are formed for most simple diffusion pump

systems to handle.

At moderate temperatures, Jacko (22) has found that if the surface effects are reduced the toluene carrier technique may still be usefully employed. The toluene still performs its essential function of reducing the attack on the parent substance (23).

Although this technique is very useful it does have certain limitations. First, it cannot be used for the determination of dissociation energies greater than D(C – H) in toluene. Second, to prevent interference from the decomposition of toluene itself, the dissociation energy to be measured should be at least 10 kcal $mole^{-1}$ less than that in toluene. Third, the radicals produced should be sufficiently reactive to produce benzyl radicals from toluene and they should be produced at a temperature high enough for the reaction to be rapid. Fourth, for the complete establishment of the validity of the results, the complete mechanism of the reaction involved should be unambiguously determined in each case.

Previous Pyrolysis Studies

There have been both static and flow system studies carried out on the Group IIB alkyls.

The pyrolysis of dimethyl zinc was studied in a toluene carrier flow system by Price and Trotman-Dickenson (1). It was originally assumed by these workers that the reaction

would closely parallel the schemes evolved in their study of the other Group IIB alkyls (2). Their proposed reaction was as follows:

$$Zn(CH_3)_2 \longrightarrow ZnCH_3 + CH_3 \qquad [1]$$

$$ZnCH_3 \longrightarrow Zn + CH_3 \qquad [2]$$

$$CH_3 + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \qquad [3]$$

$$2CH_3 \longrightarrow C_2H_6 \qquad [4]$$

$$2C_6H_5CH_2 \longrightarrow (C_6H_5CH_2)_2 \qquad [5]$$

In the previous work (2) the XCH_3 radical formed decomposed so rapidly that it was assumed that two methyl radicals were formed from each molecule that underwent reaction [1]. In this case, even at 670°C reaction [2] did not occur to any appreciable extent. Only at temperatures exceeding 730°C did reaction [2] contribute appreciably as a source of methyl radicals.

It was therefore decided to treat the decompositions of dimethyl zinc and methyl zinc as consecutive reactions.

At the higher temperatures studied, all the $Zn(CH_3)_2$ was converted to $ZnCH_3$ in a very short time and the rate of decomposition of $ZnCH_3$ was then studied. At these high temperatures, there was some interference from the decomposition of toluene itself but corrections were made based on the pyrolysis of pure toluene carried out by Szwarc (19).

At low temperatures, the decomposition of zinc methyl was assumed to be negligible and the dimethyl zinc dissociation was studied as a unimolecular reaction yielding one methyl radical.

At intermediate temperatures the rates were studied by applying consecutive rate equations.

It was found that the rate constants k_1 and k_2 were markedly dependent on the total pressure of the system. This effect was reported to be a true effect and not due to heterogeneous reaction, as packing the reaction vessel to increase the surface to volume ratio by a factor of five had no appreciable effect on the rates of the reactions. Due to the limitations of the system employed, no attempt was made to reach a pressure independent region, and all results were corrected to a selected pressure.

It was also reported that at a fixed temperature and pressure the rate constants for reaction [1] and reaction [2] in the proposed scheme were independent of large substrate concentration changes.

The effect of changing the contact time in the lower temperature region had no appreciable effect on the rate constant.

At higher temperatures the large amount of hydrogen formed was not all attributed to the decomposition of toluene. Also mentioned as a possible source of the hydrogen was the decomposition of ethane formed in the course of the

reaction.

$$CH_3 + C_2H_6 \longrightarrow C_2H_5 + CH_4$$

$$C_2H_5 \longrightarrow C_2H_4 + H$$

$$H + C_6H_5CH_3 \longrightarrow H_2 + C_6H_5CH_2$$

Also, there may have been some decomposition of dibenzyl and benzyl radicals.

The results of this investigation were as follows:

at 16 millimetres pressure:

for k_1 - $E = 47.2 \pm 1$ kcal mole^{-1},

$\log A = 11.25$;

for k_2 - $E = 35$ kcal mole^{-1},

$\log A = 6.86$;

at 5 millimetres pressure:

for k_1 - $E = 47.3$ kcal mole^{-1},

$\log A = 11.03$.

The temperature range studied was from 597°C to 825°C.

There have been three previous studies of the pyrolysis of dimethyl cadmium reported. The first of these studies appeared in 1953 (24). The work was carried out in a static system. A marked effect of the surface to volume ratio was observed, but no attempt was made to sort out the homogeneous components of the reaction. The activation energy for the overall reaction was calculated to be 28 kcal mole^{-1}.

The second investigation of the pyrolysis of dimethyl cadmium was carried out in a toluene carrier flow system (2). The progress of the reaction was followed by measuring the hydrogen, methane, ethylene and ethane formed. The reaction scheme postulated was similar to that previously described in experiments on dimethyl zinc (1). In the dimethyl cadmium study (2) it was found that reaction [1] in the scheme was the rate determining step and that reaction [2] was much faster than reaction [1]. In this investigation also, k was found to be markedly dependent on the total pressure. Experiments with dimethyl cadmium in a packed vessel indicated that the decomposition was homogeneous, as the packing caused no appreciable change in the first order rate constant.

The results obtained with dimethyl cadmium were as follows:

at 18 millimetres pressure:

for k_1 - $E = 45.8 \pm 1$ kcal $mole^{-1}$,

$\log A = 11.9$.

The temperature range studied was 469°C to 571°C.

Another investigation on the pyrolysis of dimethyl cadmium was carried out by Laurie and Long (25) in a static system. They found that the rate constant of the reaction depended upon the surface to volume ratio. The reaction was then studied at one temperature using various surface to volume ratios. The rate constant of the homogeneous reaction was estimated by extrapolation to zero surface to volume ratio. The activation energy was calculated from the

rate constant for the homogeneous reaction at 258°C, assuming log A was 13.08. This gave E = 43.5 ± 1.4 kcal mole^{-1}.

There have been many investigations of the pyrolysis of mercury dimethyl using both static and flow systems.

One of the earliest investigations carried out in a static system was that of Cunningham and Taylor (26). The purpose of their work was to study the reaction

$$CH_3 + H_2 \longrightarrow CH_4 + H .$$

Dimethyl mercury was used in this study because it was a convenient source of methyl radicals.

It was found that no measurable decomposition took place until 290°C, when there was a 2% decomposition after 5 hours of heating. When the temperature was increased to 348°C, the decomposition became relatively rapid.

Analysis of the runs at 348°C showed a definite surface effect and a definite pressure effect. However, this effect was only noted and no activation energy was calculated for the decomposition.

The pyrolysis of this compound was studied in a flow system by Gowenlock, Polanyi and Warhurst (3) in 1953. The system used was a modified toluene carrier system. Gowenlock and coworkers wished to clarify the kinetics of the decomposition of mercury dimethyl by varying a large number of experimental parameters. Therefore, pyrolyses were carried out in the presence and absence of carbon dioxide, nitrogen, toluene, ethane and hydrogen; different reaction

vessels were used, a wide range of temperatures were studied, and the percentage decomposition of alkyl, the pressure of alkyl, and the concentration of foreign gases were varied. Products were quantitatively analyzed for mercury, methane, ethane, and ethylene.

It was reported that the value of the rate constant was unaltered by relatively large changes in a wide range of parameters. If the temperature, total pressure and contact time were kept constant, a change in substrate pressure by a factor of three was found to have no effect on the rate constant. Also, at constant temperature, total pressure and substrate pressure, a more than fourfold change in the contact time was found to have no effect on the rate constant.

Apart from the temperature, the only other parameter which was observed to affect the rate constant was the total pressure of the system. This pressure effect was simply noted and no further detailed discussion or experiments were carried out.

It was determined that the decomposition was largely homogeneous and over the entire range studied, obeyed first order kinetics. The observed activation energy, 51.5 kcal $mole^{-1}$, was associated with $D(CH_3 - Hg\cdots CH_3)$. Log A = 13.5. The temperature range studied was from 489°C to 552°C.

Yeddanapalli et al (27) studied this reaction in a static system, but only three temperatures were studied,

one of which was reported to be in a region of "1.5" order. Calculations of the first order rate constants from results at 305.5°C and 323.5°C gave a value of E = 50.4 kcal $mole^{-1}$.

Another study of the thermal decomposition of mercury dimethyl in a static system was carried out by Laurie and Long (28) in 1954. Analysis of the gaseous products formed were reported to show methane, ethane and ethylene. Also, there was some type of carbonaceous material invariably found on analysis. This was assumed to be the CH_2-type polymer first observed by Cunningham and Taylor (6). At all temperatures studied, the reaction products were complex and the percentage decomposition was therefore determined by measurement of the amount of undecomposed alkyl. The reaction was found to be homogeneous, and below 333°C was reported to follow first order kinetics. The activation energy for the first order process was determined to be 51.3 ± 0.5 kcal $mole^{-1}$ and was associated with $D(CH_3 - Hg\cdots CH_3)$, as $D(CH_3\cdots Hg) + D(CH_3 - Hg\cdots CH_3)$ was determined by these workers to be 56.8 kcal $mole^{-1}$. Log A = 14.3. The temperature range studied was from 294°C to 333°C.

Another flow system determination of the pyrolysis of mercury dimethyl was carried out by Price and Trotman-Dickenson (2). The system used was a toluene carrier system and the progress of the reaction was followed by measurement of hydrogen, methane, ethane and ethylene formed. The reaction was studied as a check on the work of Gowenlock et al (3).

It was reported that the rate constants were markedly dependent on the total pressure of the system. Since the apparatus used was limited in pressure range, the majority of the runs were made at a pre-selected pressure and all results were corrected to this pressure. The activation energy was determined to be 50.1 ± 1 kcal $mole^{-1}$ at 16 millimetres pressure. Log A = 13.1. The temperature range studied was from 465°C to 608°C.

Another static system decomposition of this alkyl was carried out in 1959 by Russel and Bernstein (29) in the presence and absence of cyclopentane inhibitor and inert gases. A conventional high vacuum static system was used, but it was reported that the reaction vessel had to be pre-conditioned by a number of runs before reproducible results were obtained. The results with the alkyl alone were reported to be very complex and some doubt was cast on previous static system measurements because of this complexity. With cyclopentane inhibitor the products were reported to be much less complex. To study the total pressure effect, CO_2 and SF_6 gases were introduced in known amounts into the reaction vessel. It was found that at any given temperature the two variables affecting the rate constant were the ratio of alkyl to inhibitor and the total pressure of the system. By using CO_2 or SF_6 gas and the inhibitor along with the alkyl, a pressure independent region of rate constants was reached above 100 millimetres pressure, and a plot of these

rate constants gave an activation energy of 57.9 ± 1.4 kcal $mole^{-1}$. Log A = 15.7. The temperature range studied was from 290°C to 376°C.

One of the primary aims of the present research was to carry out experiments at high enough pressures so that the activation energies and the rate constants determined would be pressure independent. Benzene rather than toluene was therefore chosen as the carrier gas. It satisfies the basic requirements of the toluene carrier but has a substantially higher vapour pressure than toluene for any given temperature. Low temperatures could therefore be used on the heated inlet and outlet portions of the flow system, thus prolonging the effective life of ground taps and joints.

C H A P T E R I I

EXPERIMENTAL TECHNIQUE

Apparatus and Procedure

A schematic diagram of the benzene carrier gas flow system used in this research is shown in Figure 2. Reservoir R_1 contained the bulk of the alkyl, which, after trap to trap degassing, was stored at -72°C. Figure 4 shows the alkyl injection system used. The supply of alkyl for immediate use was kept frozen down at -72°C in reservoir R_3.

Figure 3 (a) is a schematic diagram of the carrier side of the overall high vacuum system. After purification, the benzene used was distilled under vacuum into reservoir R_2 and kept there for immediate use.

The reaction vessel used was made of fused quartz with graded quartz to pyrex seals situated a few centimetres beyond the furnace ends. The actual reaction zone was 18.5 centimetres long and 170.9 cubic centimetres in volume.

The temperature of the furnace was controlled by a Sunvic Resistance Thermometer Controller Type RT2. Figure 5 (a) shows the quartz furnace block with the resistance wire windings used in the furnace makeup. The heating windings were of nichrome resistance wire. The windings were tapped at seven points so that the temperature profile

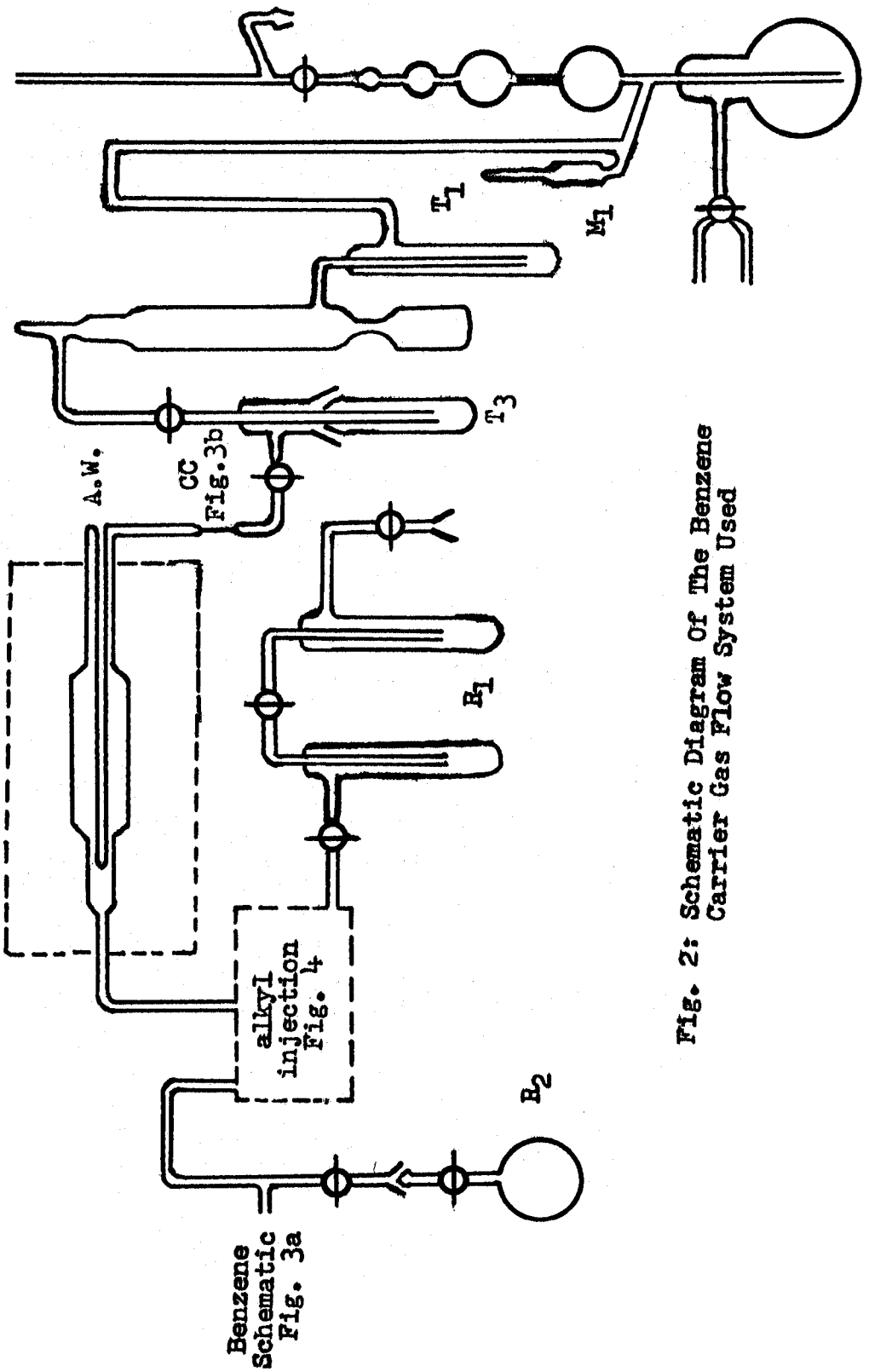


Fig. 2: Schematic Diagram Of The Benzene Carrier Gas Flow System Used

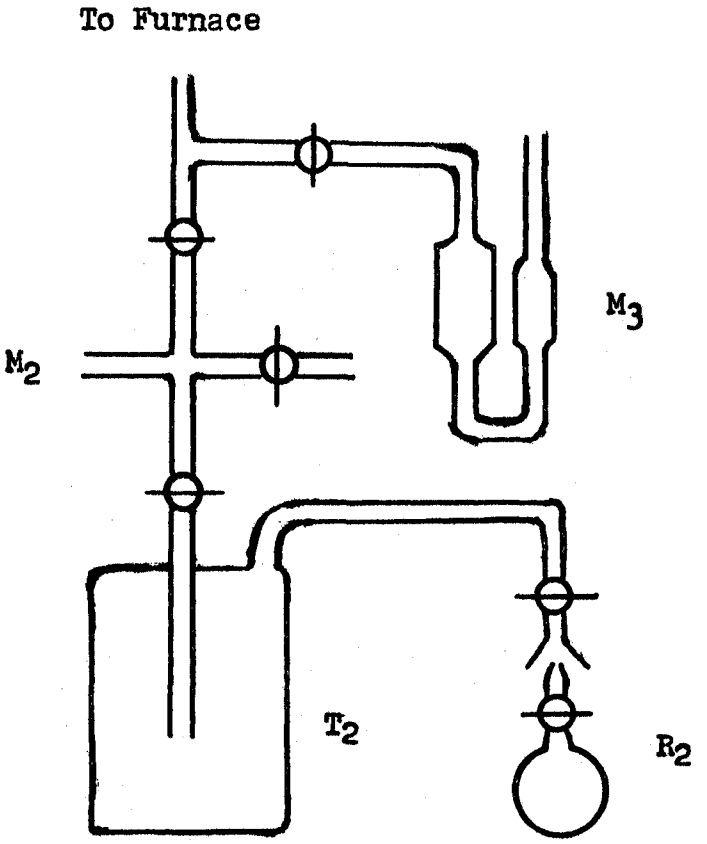


Fig. 3a: Benzene Schematic.

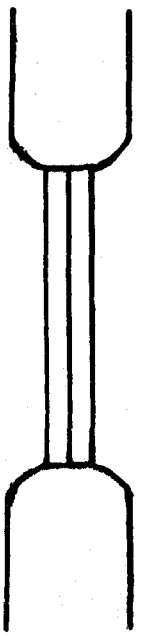


Fig. 3b: Outlet Capillary.

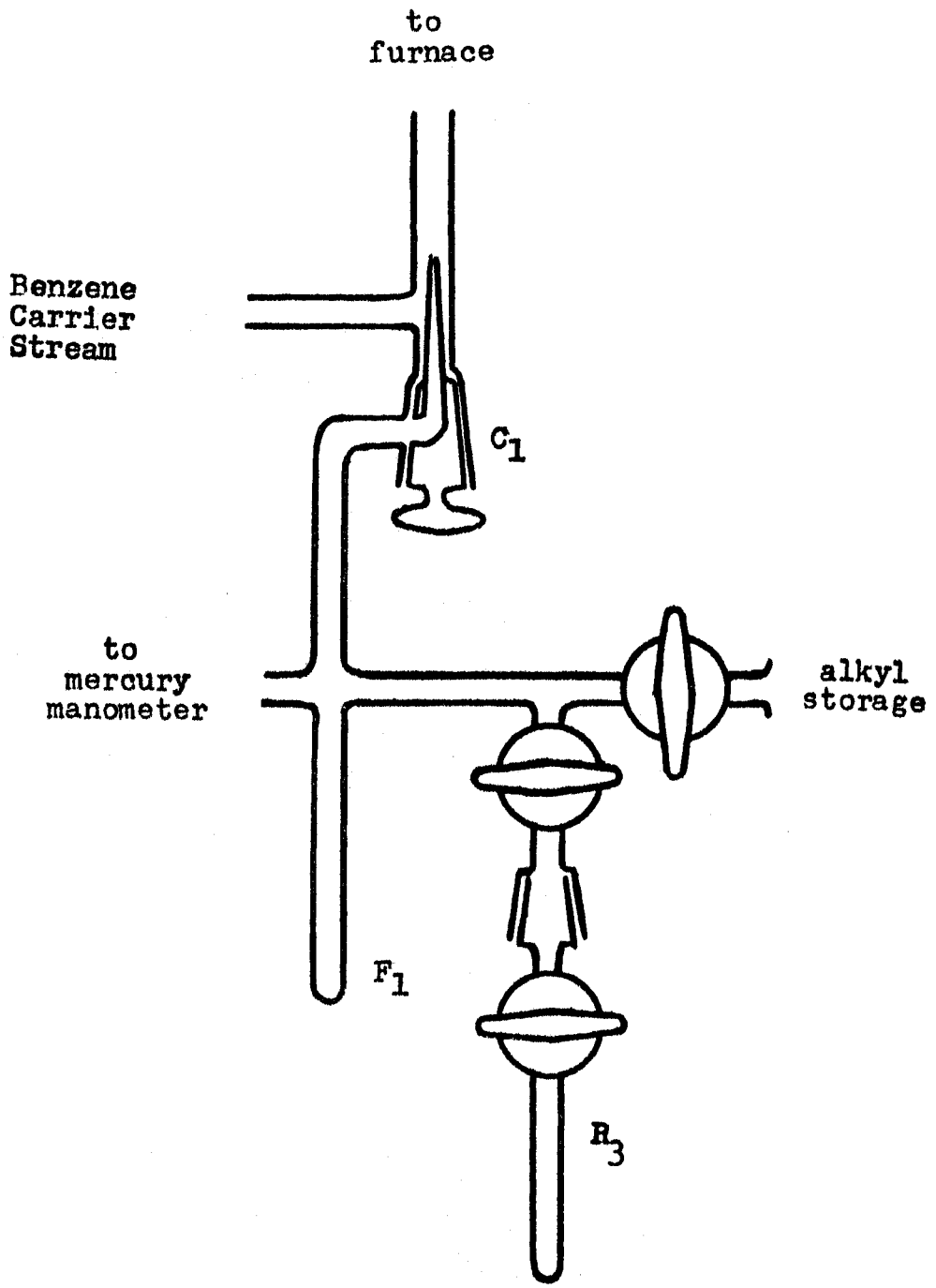


Fig. 4: Alkyl Injection System.

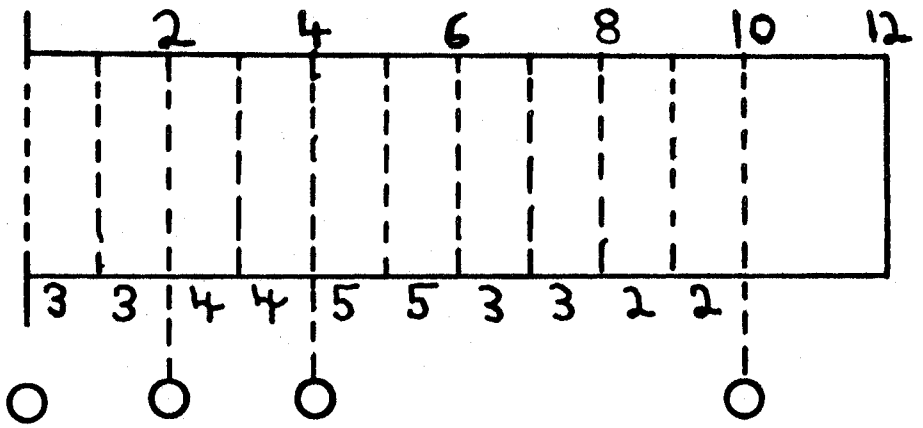


Fig. 5a: Furnace Block With Taps For Changing Temperature Profile

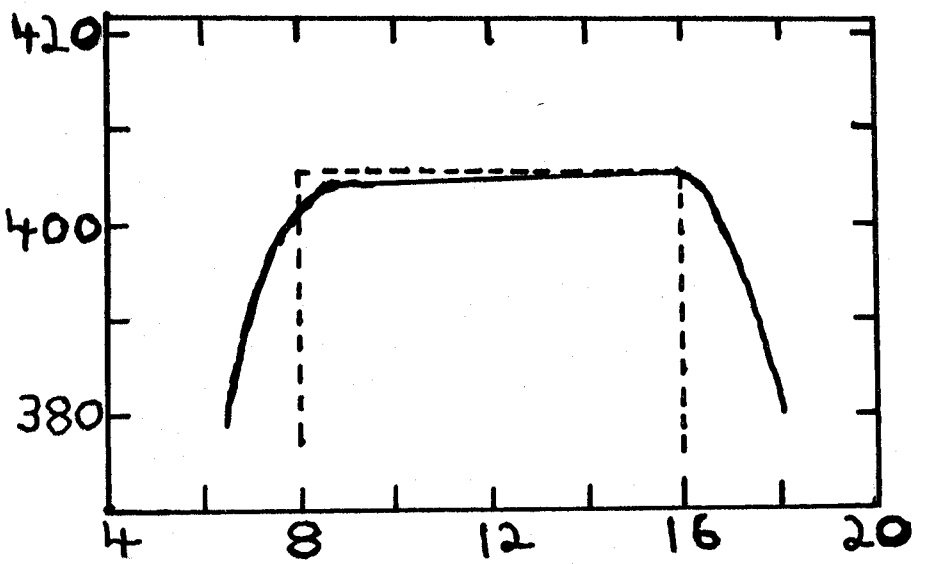


Fig. 5b: Typical Temperature Profile (solid curve) Ideal Temperature Profile(dotted curve)

could be adjusted by shunt resistances. Temperatures were measured by a thermocouple inserted in the axial thermocouple well of the reaction vessel (A. W. in Figure 2). The thermocouples used were constructed from commercially available 20 gauge chromel-p and alumel wire. These were used in conjunction with a Multivolt Leeds and Northrup No. 8691 potentiometer. Figure 5 (b) shows a typical temperature profile obtained in the process of the research covered. The desired theoretical temperature profile is included for comparison. For the pyrolysis experiments, the thermocouple was inserted 13 inches into the well. This placed the thermocouple junction at the centre of the reaction zone. The temperature profile was so adjusted that the temperature was kept within $\pm$ 2°C with a steep falloff at either end.

The flow rate through the reaction vessel was regulated by the sealed-in capillary at the outlet end of the reaction vessel [Figure 3 (b)]. All tubing on the carrier inlet side was wound with heating windings (Chromel A asbestos covered heating wire) so that it could be heated if necessary. For the high pressure runs, the carrier inlet tubing was kept at approximately 60°C. The alkyl tubing was heated as required to prevent any alkyl condensation on the walls. The outlet side of the furnace was also wound with heating wire to beyond the capillary outlet. This region was also kept at approximately 60°C. Wherever any heating windings were

employed over taps, these taps were greased with apiezon "T" grease. Other taps and ground glass joints were greased with apiezon "N" grease or silicone grease. If the joints were removed frequently, such as for weighings, silicone grease was used.

The procedure employed in a run was essentially the same for all compounds studied, the only difference being the length of time of alkyl flow and the length of the pre-alkyl and post-alkyl benzene flow. These times depended on the total pressure in the system.

A small amount of the alkyl was distilled from R_3 to F_1 (Figure 4) and then isolated in this section by keeping all taps closed. Attempts were made to distill the same amount of alkyl into F_1 for each run. A water bath at a preset temperature was then placed around F_1 and the static pressure measured by the mercury manometer. By reference to Figures 6 and 7 both static and running pressures of the alkyl could be determined and the desired bath temperature thus selected.

For the work with cadmium dimethyl, since a slow but definite reaction occurs with mercury, a spoon gauge was used to measure the alkyl pressure. The calibration of this gauge is given in Figure 9.

Prior to each run, approximately 30 grams of benzene were degassed by distillation from R_2 to T_2 [Figure 3 (a)] with T_2 kept at a temperature of -196°C and the taps open

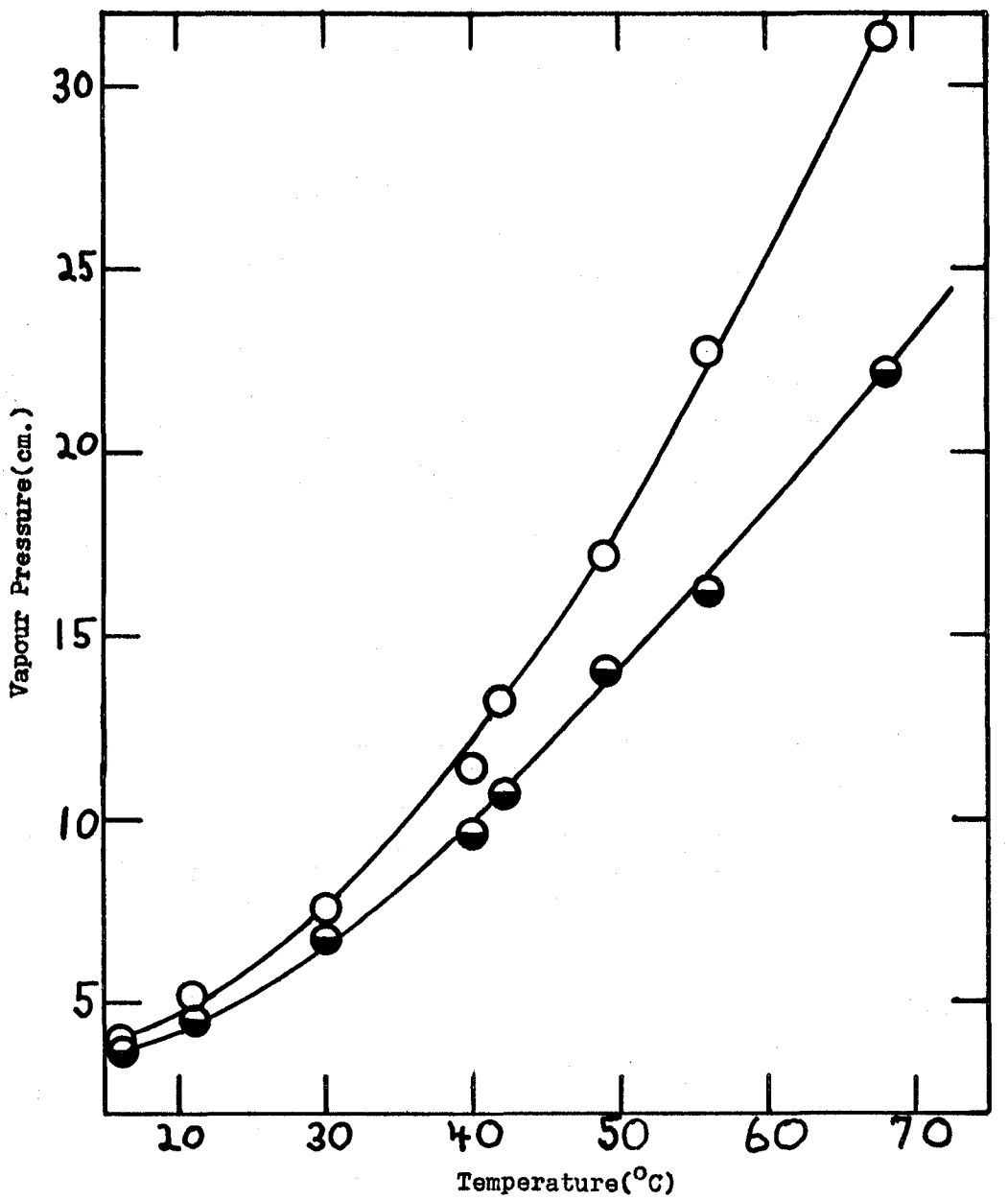


Fig. 6: Vapour Pressure Of Mercury Dimethyl
○ Static Pressure
◒ Working Pressure

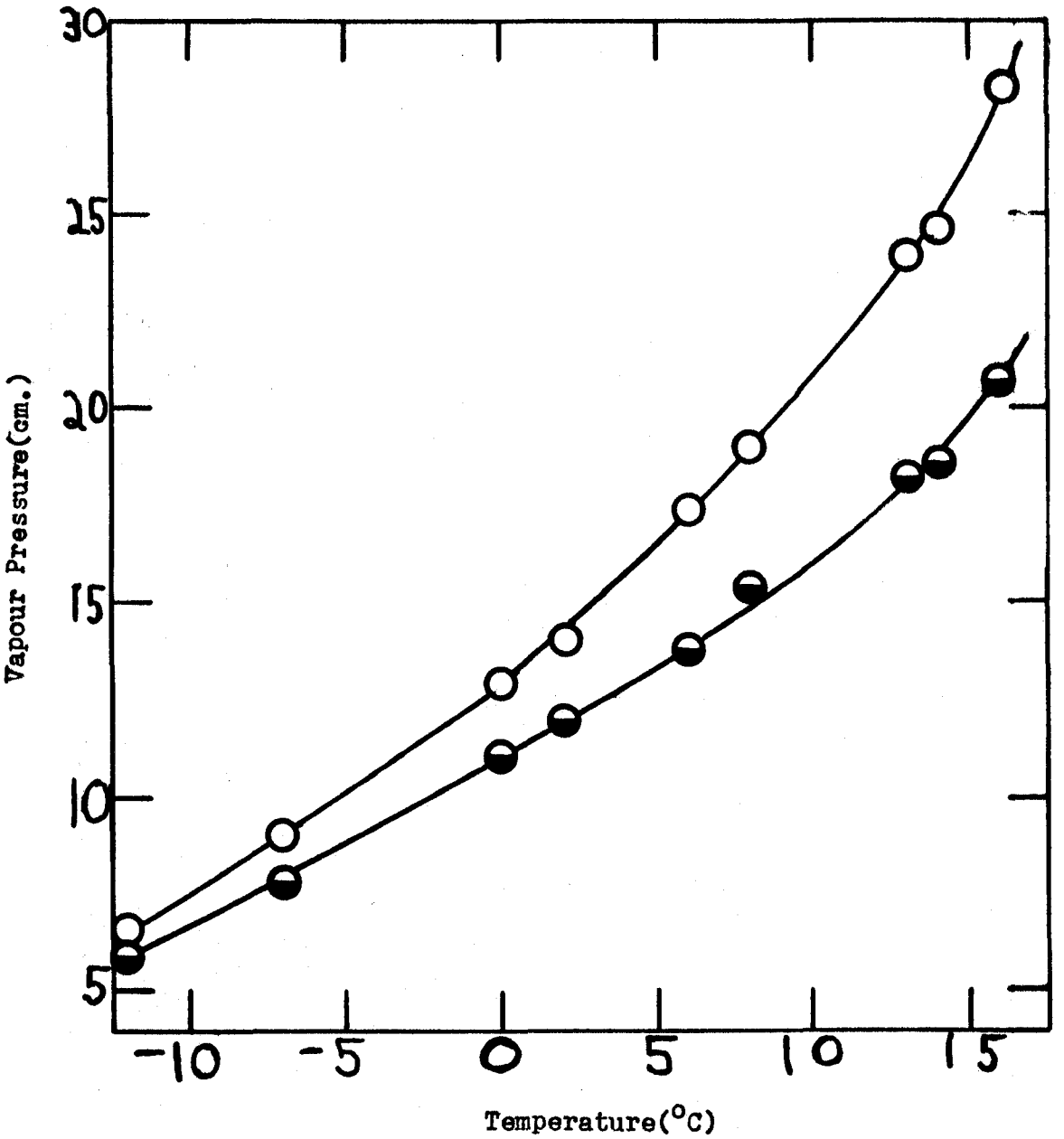


Fig. 7: Vapour Pressure Of Zinc Dimethyl
○Static Pressure
◒Working Pressure

to the high vacuum line. After this preliminary degassing, the reservoir R_2 was isolated from the system, and with all connecting taps closed, T_2 was brought to a pre-determined temperature by placing a water bath around it. This temperature for T_2 was pre-selected by reference to Figure 8, so that a preset working pressure would be kept during the course of a run. For higher pressure runs the amount of benzene used was quite large and the rate of flow (approximately 2 cubic centimetres per minute) was such that the temperature of T_2 would fall, giving a continuously decreasing running pressure. To counteract this, the bath around T_2 was equipped with an immersion heater connected to a powerstat, and the bath was continuously heated to maintain the desired running pressure. In some runs, this cooling effect was so large that the final bath temperature was 5 to 7 degrees above the initial temperature.

With all conditions now set, the flow of benzene was commenced and the running pressure measured on M_2 (for high pressure runs) and on M_3 (for runs below 4 centimetres total pressure). After a 3 minute pre-run of benzene alone, tap C_1 was opened and the alkyl at a pressure somewhat higher than the benzene pressure, was admitted into the benzene stream. After a five minute flow of alkyl, tap C_1 was closed and a 2 minute post-run of benzene alone followed. The alkyl remaining in F_1 was re-distilled into R_3. The remaining benzene was re-distilled from T_2 to R_2. The amounts of alkyl

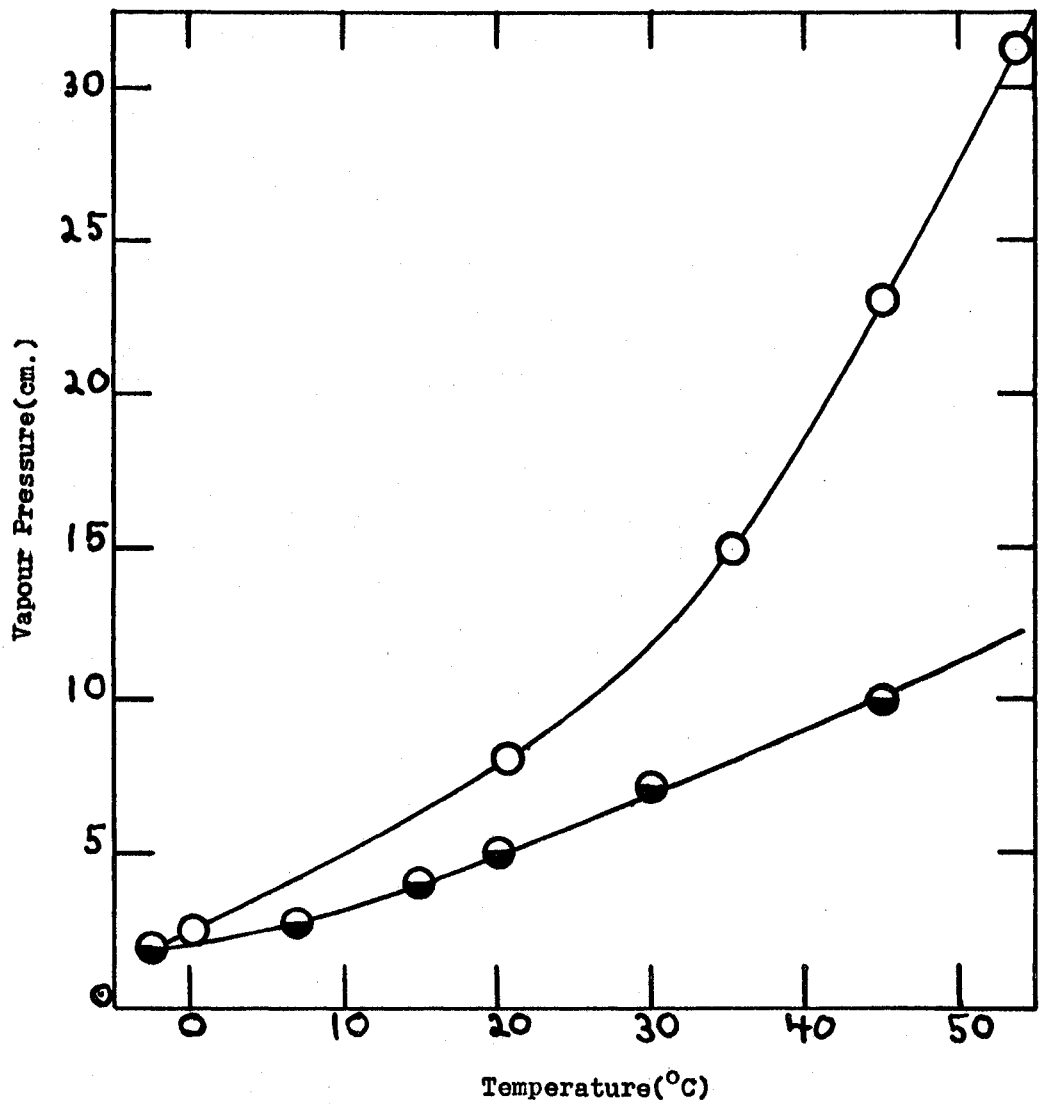


Fig. 8: Benzene Vapour Pressure
○ Static Pressure
◒ Working Pressure

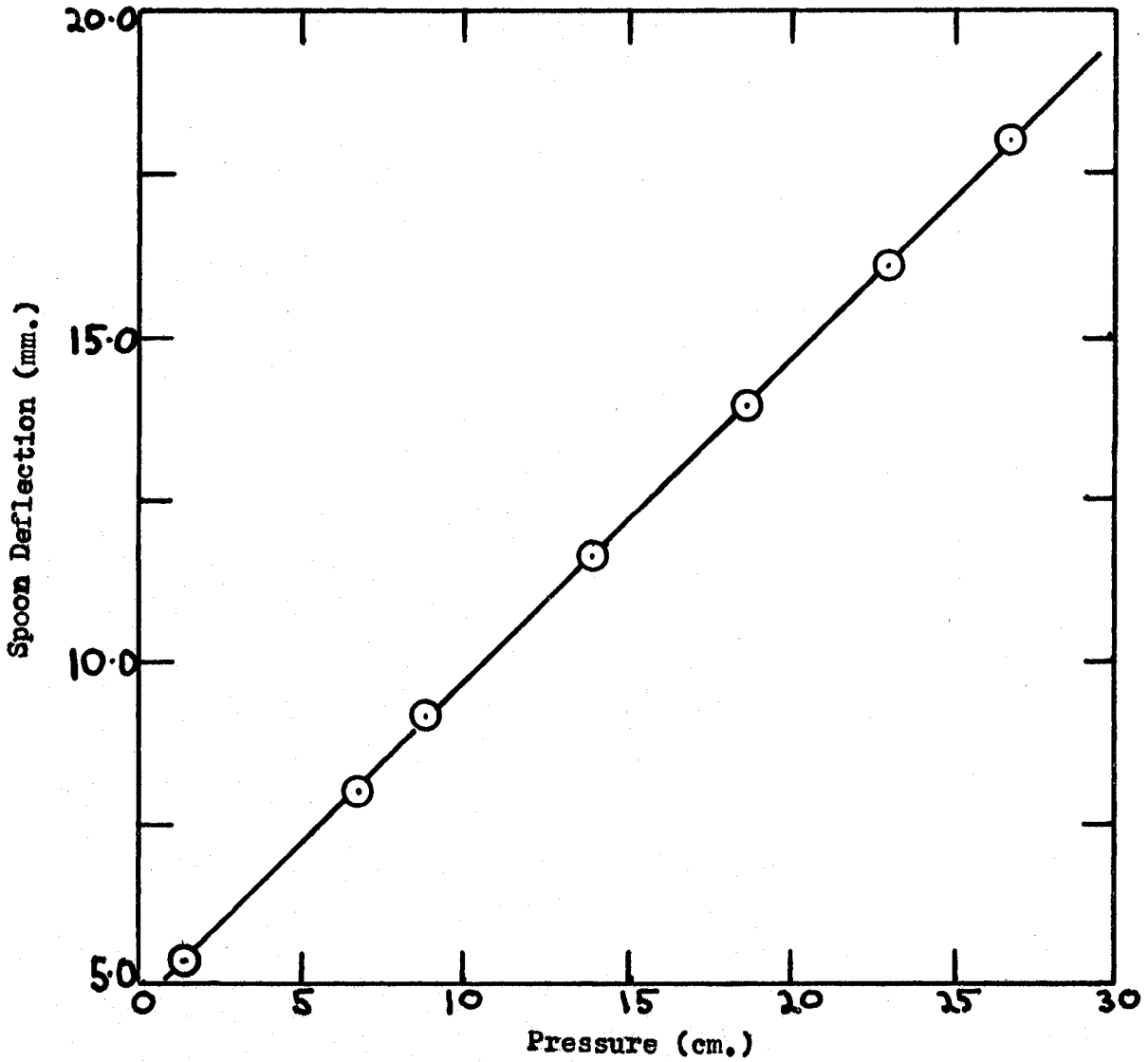


Fig. 9: Spoon Gauge Calibration

and benzene used were determined by the loss in weight of R_3 and R_2 respectively.

Trap T_3 was kept at -72°C to remove diphenyl, unreacted alkyl and benzene. A pyrex diffusion pump capable of working against a backing pressure of several centimetres transferred the remaining gaseous products to the analysis system.

Trap T_1 was a temperature-controlled trap (Leroy still) kept at a temperature of -150°C. Any remaining traces of benzene or alkyl were trapped in T_1 while the remaining gases (methane, ethane, ethylene and propane) were continually transferred to the gas burette by means of a Toepler pump. A small McLeod gauge (M_1) was used to indicate complete transfer of the gases to the gas burette. Once all the gases were in the burette the total pressure of the gases in a known volume of the burette was measured and recorded. The gases were then transferred to an evacuated sample vessel and sealed off under vacuum. The vessels were numbered and stored for subsequent analysis by vapour phase chromatography.

For all high pressure runs, static alkyl and carrier pressures were taken at time zero, running alkyl pressures were recorded every 2 minutes, and the carrier working pressure every minute. At lower pressures and longer run times, these readings were correspondingly altered.

It was found during the course of some high pressure runs that the temperature of the furnace would fall slightly

because of the cooling effect of the benzene flow. To counteract this, the controller setting was raised 2 to 3 divisions immediately prior to benzene flow commencement. Also, the temperature of the furnace was taken every 2 minutes and then averaged over the entire run period.

The gas phase chromatography unit used for analysis of the product gases was a Perkin Elmer model 154. The detector in the instrument was of the thermal conductivity type. The column used for gas analysis in the study of mercury dimethyl was a 1 meter silica gel column kept at 40°C using a helium flow of approximately 20 cubic centimetres per minute. In subsequent work a column temperature of 80°C was used. A schematic diagram of the gas injection analysis system used in conjunction with this instrument is shown in Figure 10.

The portion of the sample vessel above the break-seal was evacuated by opening the taps to the high vacuum manifold. This was done with the two-way tap C_3 open to the helium flow and isolated from the system, so that the helium flow bypassed the system and immediately went to the column. At the same time, two-way tap C_2 was opened to the "U" tube and the gas burette. Therefore the entire system, from C_3 back through the gas burette to S_1 was being evacuated. When the McLeod gauge M_4 indicated a good vacuum, C_2 was closed to the system and the system was isolated from the high vacuum. By dropping a small steel bar onto the glass

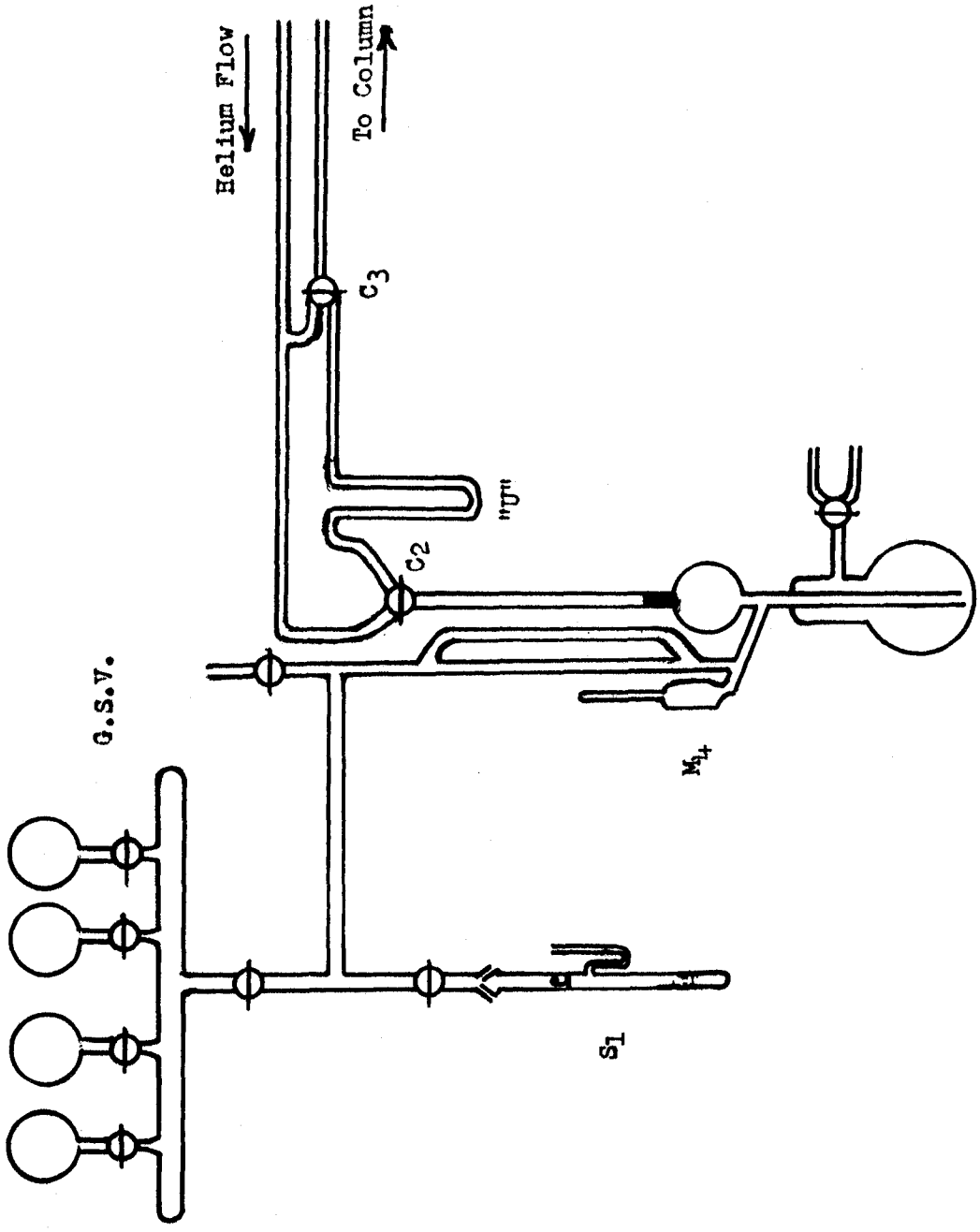


Fig. 10: Schematic Diagram Of Gas Analysis Injection System

spiral of S_1, the sample was introduced to the system and transferred to the gas burette by means of the Toepler pump. After measuring the pressure of the sample in the known volume of the gas burette, C_2 was opened and the sample forced into the "U" tube by raising the mercury level in the gas burette to tap C_2. C_2 was turned so that helium flowed into the "U" tube and simultaneously C_3 was opened to the "U" tube and the column. The helium flow then carried the sample into the column for analysis. The elution times for the various components were known from prior calibrations with the pure gases. From a knowledge of the elution times of the gases and the standard calibration curves for the pure substances, the concentration of each component was readily determined. Figure 6 shows the gas storage volumes where the pure gases were kept for calibration purposes and for determination of elution times.

For cadmium dimethyl and zinc dimethyl, analyses were carried out on the liquid samples trapped in T_3 (Figure 2). Analyses were carried out on the same chromatography instrument, using a 1 metre column of diisodecyl phthalate on diatomaceous earth kept at 120°C with a helium flow rate of approximately 15 cubic centimetres per minute. The liquid sample was injected into the helium stream using a syringe. A 10 microlitre sample of the liquid was injected per analysis.

The first order rate constants were calculated from the equation

$$k = \frac{2.303}{t_c} \log \frac{100}{100 - x}$$

where x represents the percentage of the alkyl decomposed and the contact time t_c is given by the expression

$$t_c = \frac{V \times P \times 273}{R \times T \times 760 \times 22416} \text{ sec.}$$

In the previous expression,

V = volume of the reaction zone in cubic centimetres (171 cc);

P = pressure in the reaction vessel in millimetres;

T = temperature of the reaction zone in degrees absolute;

R = total rate of flow through the reaction vessel in moles per second

$$= \frac{\text{(weight of benzene used in run)}}{\text{(molecular weight of benzene) (flow time in seconds)}}.$$

Preparation of Materials

(i) Benzene

The benzene used was Fisher Certified spectrograde benzene. Before use, it was refluxed over sodium ribbon for 24 hours and then degassed twice by bulb to bulb distillation. Also, it was freshly degassed prior to each run.

(ii) Dimethyl Mercury

Thirty grams of magnesium turnings and a few crystals of iodine were placed into a 2000 ml 3-necked flask fitted with an efficient stirrer, dual condensers and closed to the atmosphere [see Figure 11 (a)]. The system was flushed

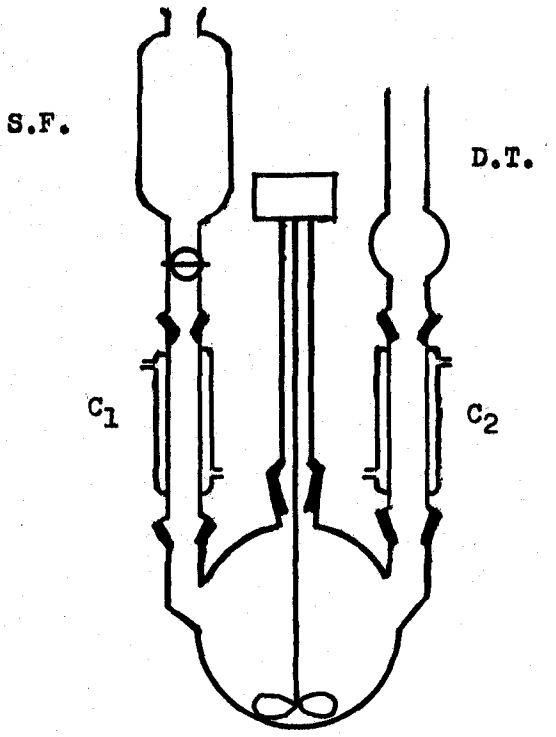


Fig. 11a: Experimental Setup For Alkyl Preps.

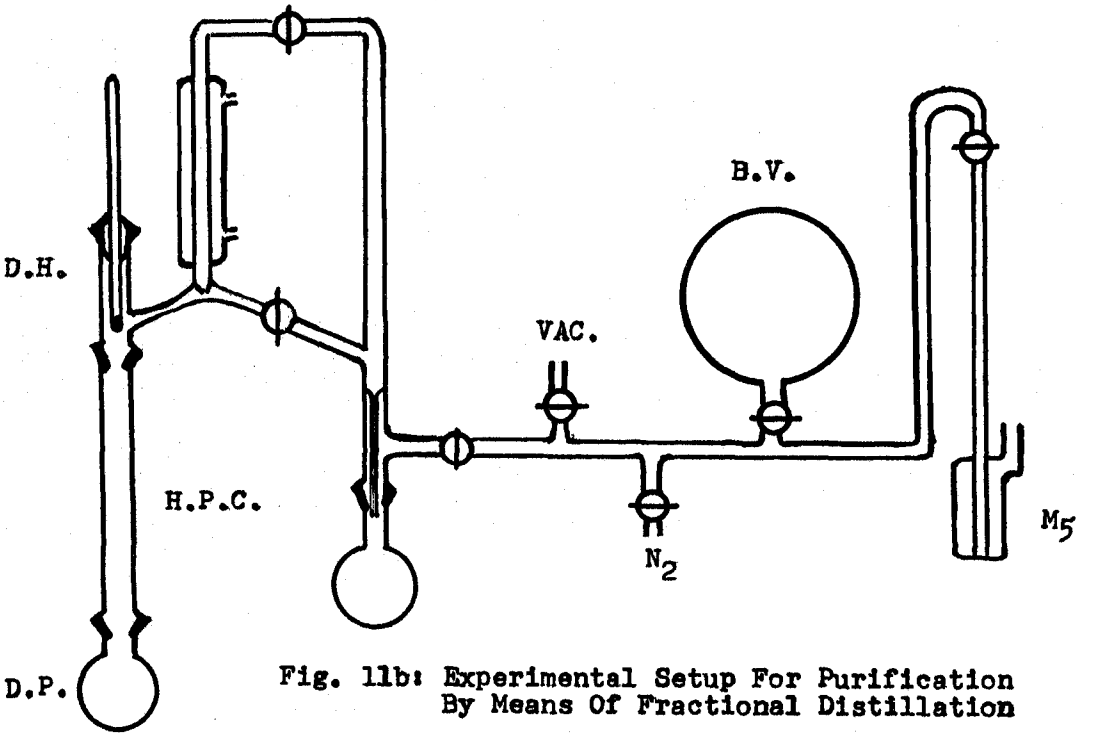


Fig. 11b: Experimental Setup For Purification By Means Of Fractional Distillation

with nitrogen and 500 mls of ethyl ether previously dried over sodium ribbon were added to the flask. Vigorous stirring was started and 79 mls of methyl iodide was added dropwise from a separatory funnel atop one of the condensers. The methyl iodide was previously refluxed over 10-15 grams of silver hydroxide and then redistilled. The Grignard was refluxed for one hour after all the methyl iodide was added. This methyl magnesium iodide slurry was then put into a separatory funnel atop a similarly equipped 3-necked flask and added dropwise over a 60 minute period to an ether slurry of 130 grams of mercuric chloride. The mercuric chloride had been previously oven dried at 120°C and then left in a desiccator overnight. The mixture was refluxed for an additional three hours and then cooled in ice, and the excess Grignard hydrolyzed by the slow addition of 250 mls of water. The ether layer was separated, washed with two 25 ml portions of water, and dried over 10 grams of anhydrous calcium chloride. Most of the ether was stripped by evaporation under reduced pressure and the remaining solution was fractionally distilled using the apparatus shown in Figure 11 (b). The fraction boiling at 92°C at 750 mm was collected and stored under its own vapour pressure at -78°C.

(iii) Cadmium Dimethyl

The methyl magnesium iodide Grignard was made exactly as for the case of mercury dimethyl. The Grignard slurry was then added to 33 grams of cadmium chloride in an ether

slurry. The cadmium chloride had been previously dried in an oven at 120°C and cooled in a desiccator. Addition took place over a three hour period. The reaction mixture was allowed to reflux overnight. The ether solution of cadmium dimethyl was separated into a distilling flask and the residue in the flask was twice extracted with 150 mls of ether. The bulk of the ether was then stripped off under reduced pressure and a nitrogen atmosphere. The ether came over at about 30°C. The remainder of the solution was then fractionally distilled under a nitrogen atmosphere and reduced pressure [see Figure 11 (b)]. The fraction with b.p. 105°C at 754 mm Hg was collected and stored under its own vapour pressure at -78°C.

(iv) Zinc Dimethyl

Thirty grams of dimethyl mercury and 35.8 grams of Zn metal were refluxed in apparatus [see Figure 11 (b)] under a nitrogen atmosphere and under slightly reduced pressure. The zinc used was Fisher A.C.S. grade granular zinc metal, 20 mesh. After about 15 hours of reflux, temperature at the fraction head was 40°C without any heat applied to the packed column. An initial fraction of about 3 grams of zinc dimethyl was taken at this time, and then the mixture allowed to reflux further. After another 12-14 hours of reflux, a second fraction with b.p. 40°C was removed. The total amount of alkyl obtained was 7.62 grams, giving an overall yield of 61.2%.

CHAPTER III

EXPERIMENTS AND RESULTS

Mercury Dimethyl

The complete experimental results are given in Table 1. These results may be represented by a mechanism similar to that previously proposed for the decomposition of dimethyl mercury in the presence of toluene (2):

$$Hg(CH_3)_2 \longrightarrow HgCH_3 + CH_3 \qquad [1]$$

$$HgCH_3 \longrightarrow Hg + CH_3 \qquad [2]$$

$$CH_3 + C_6H_6 \longrightarrow CH_4 + C_6H_5 \qquad [3]$$

$$2CH_3 \longrightarrow C_2H_6 \qquad [4]$$

$$2C_6H_5 \longrightarrow C_{12}H_{10} \qquad [5]$$

The rate constants were calculated from the usual first order equation assuming that the number of moles of ethane plus half the number of moles of methane formed during a run should be equal to the number of moles of the alkyl decomposed.

To test for possible side reactions such as

$$CH_3 + C_6H_5 \longrightarrow C_6H_5CH_3 \qquad [6]$$

runs were carried out under the unfavourable conditions of low benzene pressure and high temperature. When corrected

TABLE I

Pyrolysis of dimethyl mercury

Temp. (° K)	Contact time (sec)	Total pressure (cm)	Length of run (min)		$Hg(Me)_2$ (10^{-4} mole)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)	k (sec^{-1})
			Total	Alkyl				
800	1.10	21.8	8	5	18.3	13.9	7.2	1.35
799	0.89	15.4	8	5	8.06	5.47	2.23	1.10
800	1.06	13.0	8	5	6.05	4.41	2.16	1.20
800	1.45	8.0	20	10	5.47	3.23	2.78	1.13
798	1.18	7.4	8	5	5.17	3.58	2.26	1.30
784	1.09	26.0	8	5	20.4	8.42	3.67	0.617
784	1.09	18.6	8	5	15.3	7.17	4.17	0.642
784	1.14	10.6	8	5	24.2	9.54	6.94	0.579
783	1.18	8.0	8	5	13.7	5.13	4.72	0.644
784	1.17	7.8	8	5	13.5	5.01	4.72	0.653
783.5	1.65	2.9	20	15	16.3	3.74	4.89	0.348
783.5	1.53	2.8	20	15	20.8	5.15	7.68	0.376
783	1.83	2.3	20	15	6.2	2.03	1.81	0.333
783.5	2.46	1.89	20	15	5.42	1.43	1.64	0.243
783.5	2.90	1.10	40	30	6.95	2.78	4.03	0.212
783	3.06	1.05	20	15	6.42	1.29	2.10	0.182
771	1.04	13.44	8	5	10.89	3.30	1.897	0.378
771	1.04	12.36	8	5	10.05	3.095	1.502	0.348
760	1.19	15.65	8	5	18.8	3.67	2.39	0.221
760	1.17	13.72	8	5	16.05	2.90	1.60	0.216
760	1.08	11.25	8	5	13.84	2.44	1.60	0.226
760	1.19	7.86	10	7	13.54	2.32	1.78	0.213
760	1.28	5.02	10	7	10.55	1.53	1.42	0.179
760	1.67	2.71	20	15	13.68	1.59	1.87	0.129
760	3.34	1.02	30	20	9.25	0.585	0.957	0.0434
760	12.42	0.36	30	20	7.82	0.772	1.398	0.0238
752	1.147	10.0	8	5	11.20	1.608	0.828	0.1374
753	1.143	9.90	8	5	11.87	1.762	0.895	0.152
753	1.135	9.60	8	5	11.29	1.655	0.878	0.144
744	1.21	11.40	8	5	12.50	1.36	0.669	0.0939
743	1.12	10.70	10	7	12.56	1.71	0.683	0.117
724	1.158	10.6	10	7	11.54	0.565	0.2138	0.0378
723	1.187	10.4	8	5	11.02	0.426	0.1705	0.02985
724	1.158	10.3	10	7	25.24	0.856	0.453	0.03108
724	1.124	9.8	10	7	14.1	0.658	0.284	0.0395
723	1.16	9.4	8	5	12.47	0.462	0.182	0.02908
720	1.14	12.74	8	5	15.75	0.538	0.223	0.0282
720	1.13	10.0	10	7	18.02	0.651	0.297	0.0304
720	1.235	7.9	15	10	13.95	0.506	0.193	0.0261
720	1.126	5.4	20	15	13.64	0.454	0.225	0.0285
720	2.018	2.48	20	17	6.21	0.168	0.115	0.01595
720	8.89	0.41	30	20	7.13	0.197	0.233	0.0117
708	1.17	12.20	10	7	15.74	0.328	0.135	0.0163
706	1.098	17.8	8	5	5.68	1.183	0.250	0.01362
706	1.12	11.8	8	5	11.90	0.1945	0.716	0.01358
706	1.075	11.4	8	5	12.68	0.234	0.0889	0.0152
695	1.305	14.26	12	8	24.5	0.26	0.144	0.00846
695	1.285	7.5	20	15	18.8	0.187	0.0823	0.00734
696	1.77	2.65	20	15	13.98	0.1142	0.0607	0.00468
695.5	2.02	2.00	20	15	4.73	0.0473	0.0146	0.00410
695	5.72	0.75	30	20	5.52	0.0299	0.0394	0.00173
693	1.268	9.46	10	7	17.59	0.173	0.0551	0.00636
693.5	1.278	9.12	8	5	11.8	0.101	0.0349	0.00569
693	1.255	8.80	10	7	22.35	0.135	0.0427	0.00403

for slight differences in total pressure, the first order rate constants obtained at approximately 2.5 cm at 783°K using alkyl concentrations of 6.6×10^{-9} to 20.8×10^{-9} mole cc^{-1} show little variation. Reaction [6] and similar side reactions are therefore negligible.

Figures 12, 13, 14 and 15 show the marked pressure effect on the rate constant at a constant temperature. It appears from these figures, that above 10 cm total pressure, the first order rate constant is independent of any further pressure increase.

Previous flow system studies (1,2,3) have shown that this decomposition is first order and largely homogeneous. Therefore, only the pressure and temperature effects were studied to any considerable extent in this research.

The Arrhenius plots for the high pressure limit and for 16 mm pressure are shown in Figure 16. The straight lines may be expressed respectively as

$$\log k/(sec^{-1}) = 14.8 - (53{,}700 / 2.303\ RT)$$

and

$$\log k/(sec^{-1}) = 13.6 - (51{,}000 / 2.303\ RT).$$

Cadmium Dimethyl

The experimental results for cadmium dimethyl are given in Table 2. These results may be discussed in terms of a mechanism similar to that proposed for mercury dimethyl:

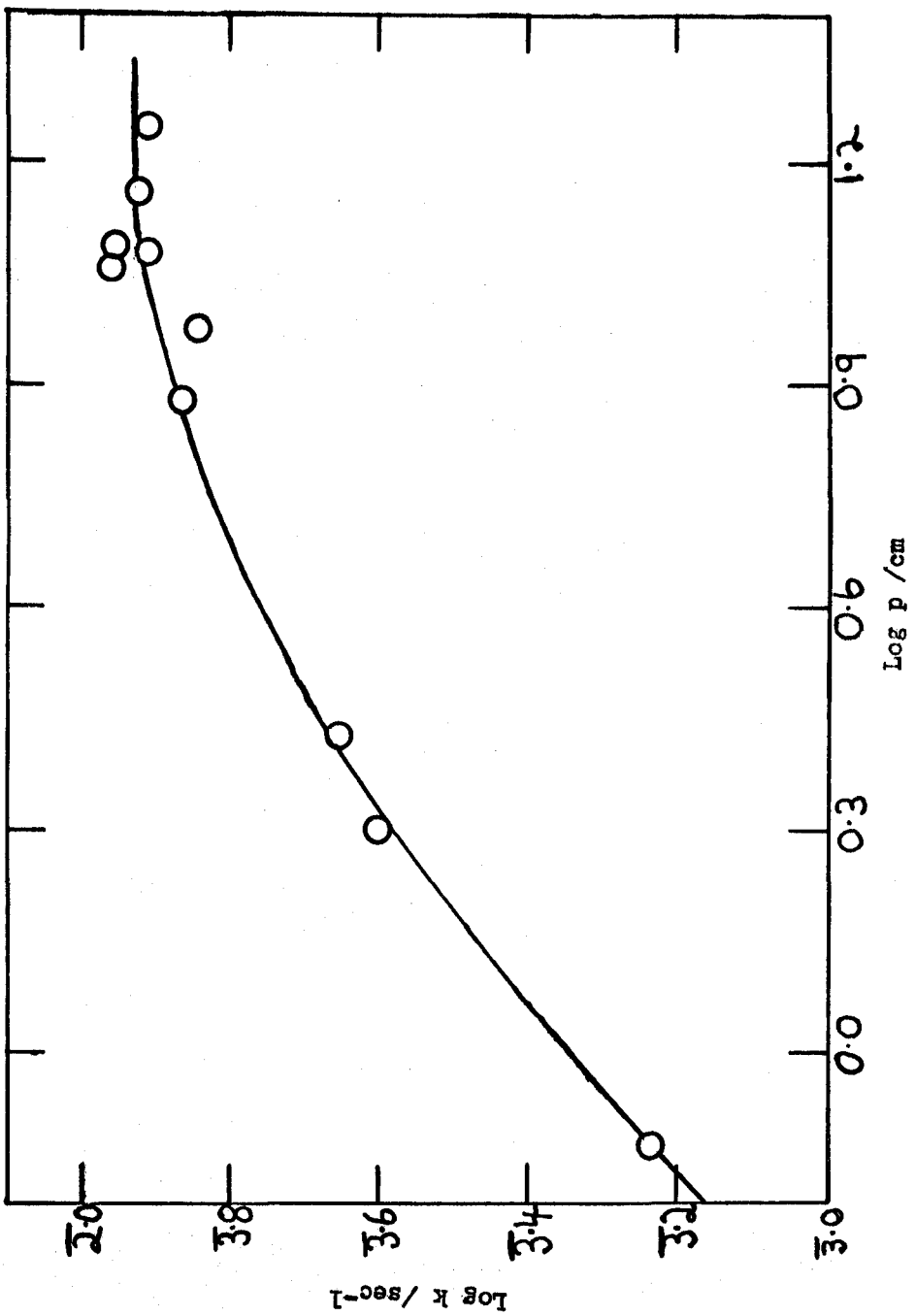


Fig. 12: The Variation Of The Rate Constant With Pressure For Mercury Dimethyl T = 695° K

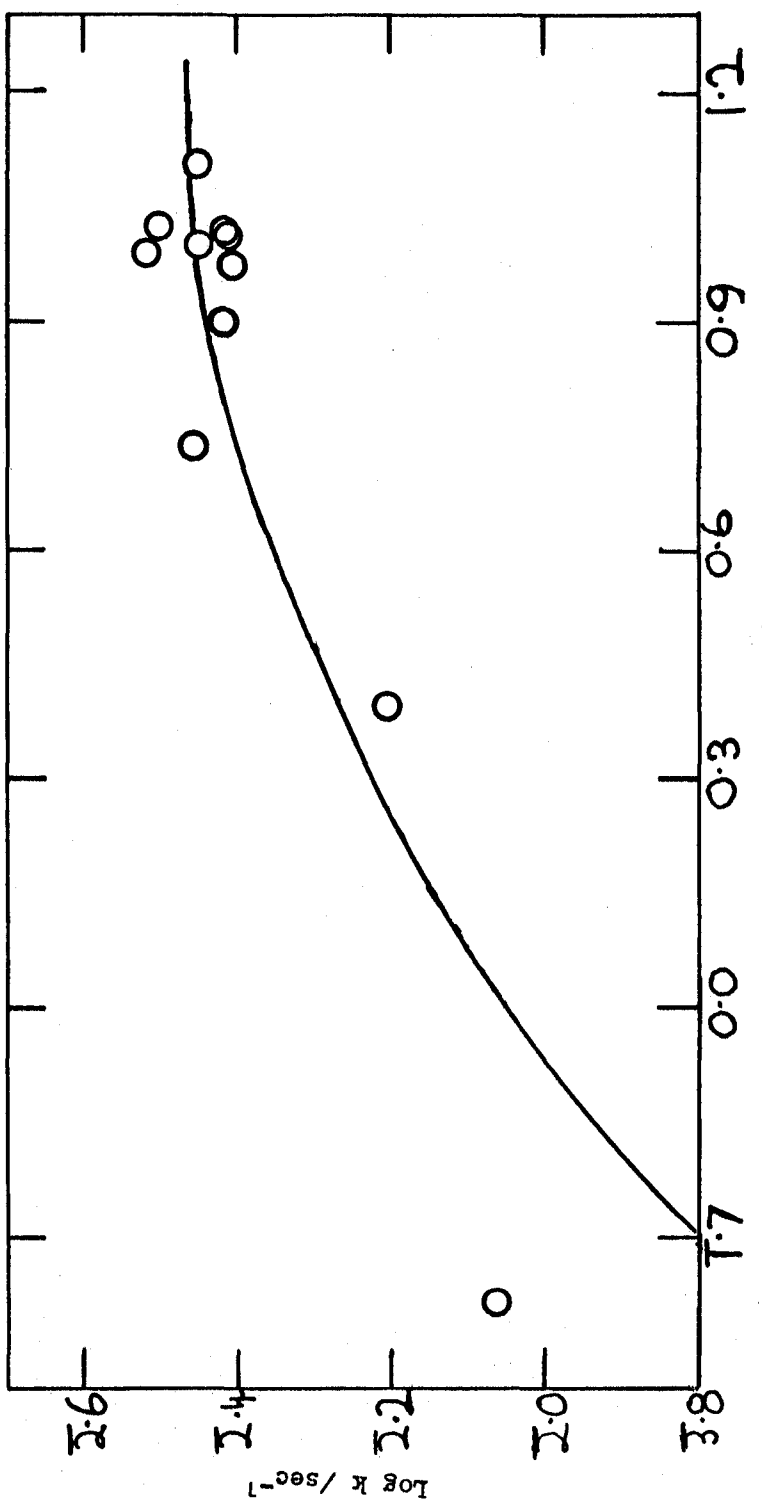


Fig. 13: The Variation Of The Rate Constant With Pressure For Mercury Dimethyl $T = 720^{0}$ K

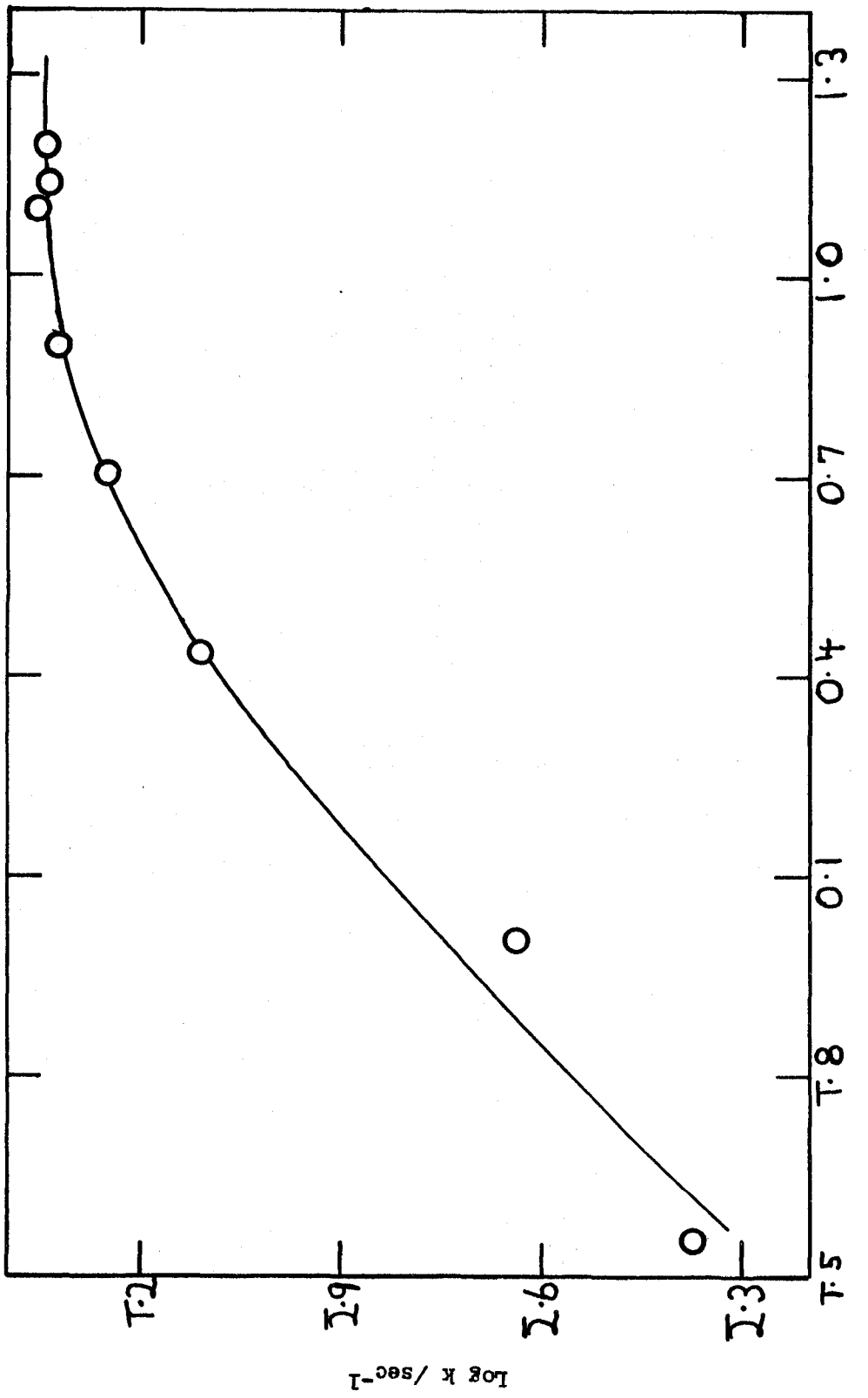


Fig. 14: The Variation Of The Rate Constant With Pressure For Mercury Dimethyl T = 760° K

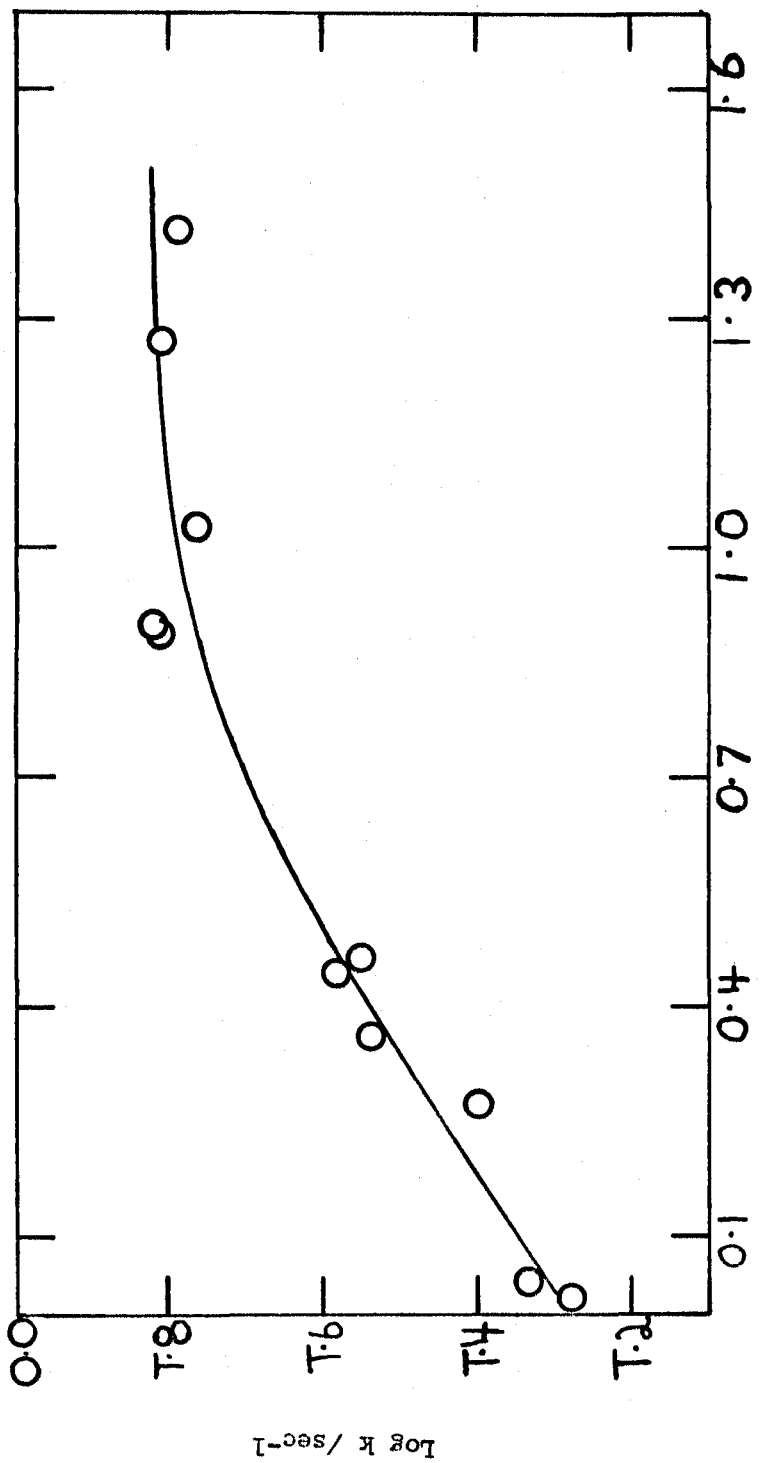


Fig. 15: The Variation Of The Rate Constant With Pressure For Mercury Dimethyl T = 784° K

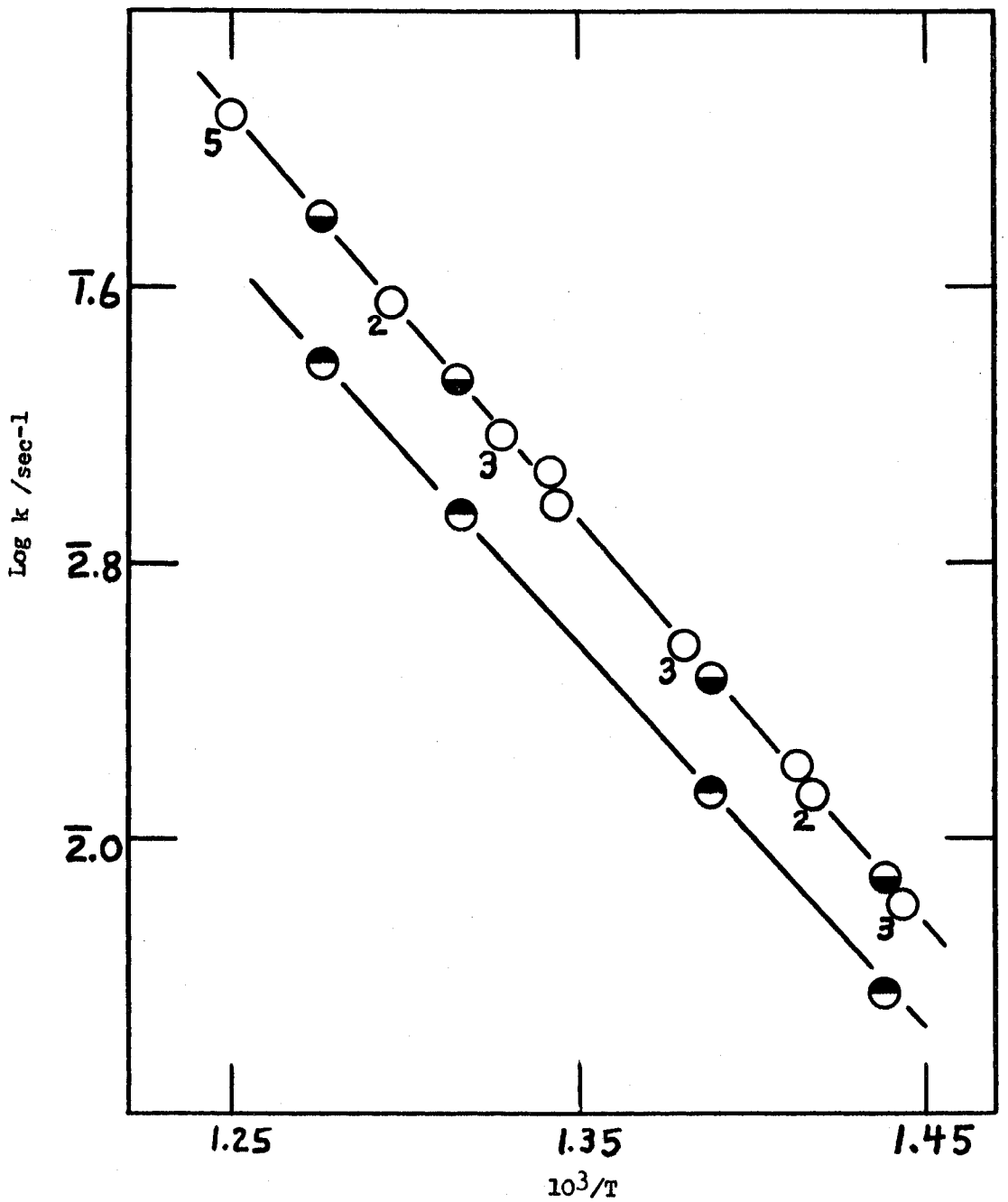


Fig. 16: Arrhenius Plots For The Decomposition Of Mercury Dimethyl At The High-Pressure Limit(○, ◒) And At 16mm Pressure(◓). Subscripts Refer To Number Of Experiments Averaged To Obtain A Point. Half-filled Circles Are Points Taken From Log K Verses Log P Curves.

TABLE 2

Pyrolysis of Dimethyl Cadmium

Temp. (°K)	Contact time (sec)	Total press. (cm)	Length of run (min) Total	Alkyl	$Cd(Me)_2$ (10^{-4} mole)	CH_4 (10^{-4} mole)	C_2H_6 (10^{-4} mole)	C_2H_4 (10^{-6} mole)	C_3H_8 (10^{-6} mole)	toluene (10^{-5} mole)	k (sec^{-1})
798	1.07	11.12	8	5	9.27	6.14	3.14	8.12	3.21	4.45	1.05
797.5	1.04	10.60	8	5	9.68	5.82	3.18	6.40	8.70	7.56	1.02
799	1.23	8.80	8	5	18.2	8.40	7.85	20.9	14.40	10.22	0.971
799	1.15	8.80	8	5	7.51	4.72	2.77	6.11	6.11	5.50	1.05
799	1.21	8.48	8	5	7.36	4.08	3.56	12.8	36.0	3.60	1.18
799	1.23	7.48	8	5	11.22	6.24	4.83	11.7	13.1	8.12	1.11
799	1.13	6.28	8	5	4.63	3.09	1.89	1.0	1.0	3.99	1.14
797	1.41	4.60	25	15	10.80	6.53	4.64	9.44	8.64	6.27	0.959
800	2.20	2.61	60	50	16.99	7.38	7.63	15.42	15.42	12.61	0.563
799	2.02	2.12	80	60	16.29	7.89	6.70	16.30	16.30	7.15	0.569
800.5	2.41	1.63	60	50	16.43	6.60	8.56	19.6	26.7	8.32	0.600
775	1.10	16.18	8	5	12.36	4.47	2.05	8.41	1.87	5.33	0.396
775	1.10	14.90	8	5	10.53	3.86	1.83	6.16	1.74	4.94	0.406
776	1.05	13.20	8	5	8.26	5.31	2.78	6.61	3.97	4.15	0.524
777	1.11	12.10	8	5	16.50	4.83	3.32	6.26	8.80	4.08	0.394
777	1.11	11.86	10	7	13.27	4.59	2.47	6.72	5.04	5.59	0.415
776	1.12	10.42	8	5	12.36	3.57	2.46	6.07	5.45	5.11	0.387
778	1.12	9.70	8	5	14.80	4.18	3.25	6.03	9.06	3.55	0.407
777	1.14	8.44	8	5	12.00	3.80	2.74	5.82	5.82	3.46	0.432
779	1.28	6.00	20	15	14.40	5.27	3.63	5.86	5.86	5.03	0.457
777	1.34	5.60	18	13	18.80	4.69	4.15	9.35	11.28	4.34	0.330
777	1.29	4.70	20	15	10.39	3.03	2.20	3.76	1.27	4.26	0.339
777	1.59	3.22	25	20	9.55	2.51	2.27	4.18	4.26	3.56	0.287
777	2.03	2.58	45	35	11.59	3.27	2.95	7.70	9.00	3.35	0.254
777	2.72	1.88	60	50	12.00	3.56	3.36	6.38	7.84	2.90	0.207
758	1.16	16.20	8	5	11.51	1.79	1.56	1.87	0.71	4.28	0.203
759	1.08	13.80	8	5	10.24	2.74	1.13	4.15	2.85	2.20	0.247
760.5	1.06	13.76	8	5	12.01	2.68	1.16	3.92	2.26	2.22	0.209
760	1.11	12.74	8	5	14.75	2.65	1.52	3.44	4.42	4.40	0.195
760	1.10	11.70	8	5	11.92	2.67	1.49	2.99	2.70	2.31	0.227
761	1.14	10.36	10	7	14.68	3.48	1.98	5.34	3.84	2.93	0.253
761	1.16	8.80	8	5	11.79	2.54	1.68	3.92	2.79	1.63	0.234
762	1.26	8.12	15	12	10.81	3.09	1.54	3.70	3.27	2.50	0.257
762.5	1.42	5.86	20	15	14.26	3.16	2.18	3.92	4.79	2.84	0.212
761	1.32	5.64	20	15	16.85	3.10	2.25	4.99	5.50	2.03	0.190
761	1.43	5.60	20	15	13.90	2.74	1.86	4.32	3.14	4.21	0.185
762	1.68	3.50	60	50	34.13	5.18	4.84	6.21	8.66	7.57	0.152
761	1.98	2.66	40	30	5.97	1.86	0.797	3.69	2.46	1.31	0.154
763	2.29	2.24	60	50	19.45	3.78	3.90	6.59	8.60	5.34	0.160
761	2.06	2.09	80	70	11.80	2.34	1.49	2.73	1.37	3.45	0.121
743	1.27	13.46	8	5	18.33	2.14	1.19	3.29	4.46	3.12	0.102
744	1.13	10.50	8	5	17.28	1.99	1.14	1.86	1.86	1.83	0.108
744	1.17	10.32	8	5	20.22	2.38	1.45	4.70	2.16	2.16	0.114
744	1.15	10.26	8	5	12.92	1.79	1.08	2.40	2.04	1.75	0.132
744	1.18	10.04	8	5	9.69	1.39	0.64	1.76	1.10	1.67	0.107
744	1.18	8.40	8	5	12.56	1.46	0.71	2.23	1.23	1.56	0.0898
744	1.38	5.76	13	10	9.69	1.49	0.79	1.48	1.84	0.66	0.105
746	1.27	5.46	8	5	5.48	1.297	0.578	0.78	1.09	0.838	0.158
745	1.33	5.36	20	15	14.68	1.69	0.945	1.82	2.41	1.96	0.090
745	2.31	2.27	40	30	16.57	1.58	1.32	3.75	4.56	2.11	0.0568
744	2.06	2.16	60	50	14.4	2.04	1.18	3.97	2.77	1.73	0.0749

$$Cd(CH_3)_2 \longrightarrow CdCH_3 + CH_3 \qquad [1]$$

$$CdCH_3 \longrightarrow Cd + CH_3 \qquad [2]$$

$$CH_3 + C_6H_6 \longrightarrow CH_4 + C_6H_5 \qquad [3]$$

$$2CH_3 \longrightarrow C_2H_6 \qquad [4]$$

$$2C_6H_5 \longrightarrow C_{12}H_{10} \qquad [5]$$

Here, reaction [2] is again assumed to be much faster than reaction [1]. The percentage decomposition has therefore been calculated as in the case of mercury dimethyl, by assuming that each cadmium dimethyl molecule undergoing reaction yields two methyl radicals. In this phase of the research the fate of the methyl radicals formed has been more fully investigated. A check on the extent of reaction [6]

$$CH_3 + C_6H_5 \longrightarrow C_6H_5CH_3 \qquad [6]$$

was made by analyzing the contents of the acetone dry-ice trap for toluene by gas phase chromatography. These analyses showed that reaction [6] did occur to some extent but even in cases where the ratio of carrier to alkyl was lowest, only 5% of the methyl radicals were removed by this reaction. A correction for the methyl radicals found as toluene was made throughout the cadmium dimethyl calculations but had only a small effect on the values of the rate constants. A similar correction was made for small quantities of propane. Thus the overall fraction decomposed was calculated by dividing the number of moles of ethane and ethylene, plus half the number of moles of methane plus half the number of moles of

toluene, plus three-halves the number of moles of propane by the number of moles of alkyl used. A blank correction of 3×10^{-5} moles of methyl radicals was subtracted to allow for decomposition that occurred in the alkyl finger, F_1.

Figures 17, 18, 19 and 20 show the pressure effect on the rate constant at a constant temperature. Above 10 cm there appears to be no further pressure effect.

Figure 21 shows the Arrhenius plots for the high pressure limit and for 18 mm pressure. These straight lines may be expressed respectively as:

$$\log k_1/(\text{sec}^{-1}) = 13.4 - (48{,}800 / 2.303\ RT)$$

and

$$\log k_1/(\text{sec}^{-1}) = 12.3 - (45{,}800 / 2.303\ RT).$$

Zinc Dimethyl

The experimental results obtained for zinc dimethyl have not been included in the thesis. Although more than sixty runs have been tried on this compound, the scatter in the data is such that only tentative results can presently be given. Also, packed vessel runs have shown that there may be a pronounced surface effect which was not observed in previous work (1). On decomposition of the alkyl, a white crystalline solid was observed as a deposit on the outlet tube of the furnace. On admission of air into the system, this solid changed into a yellowish substance which did not melt even at temperatures exceeding 500°C, whereas

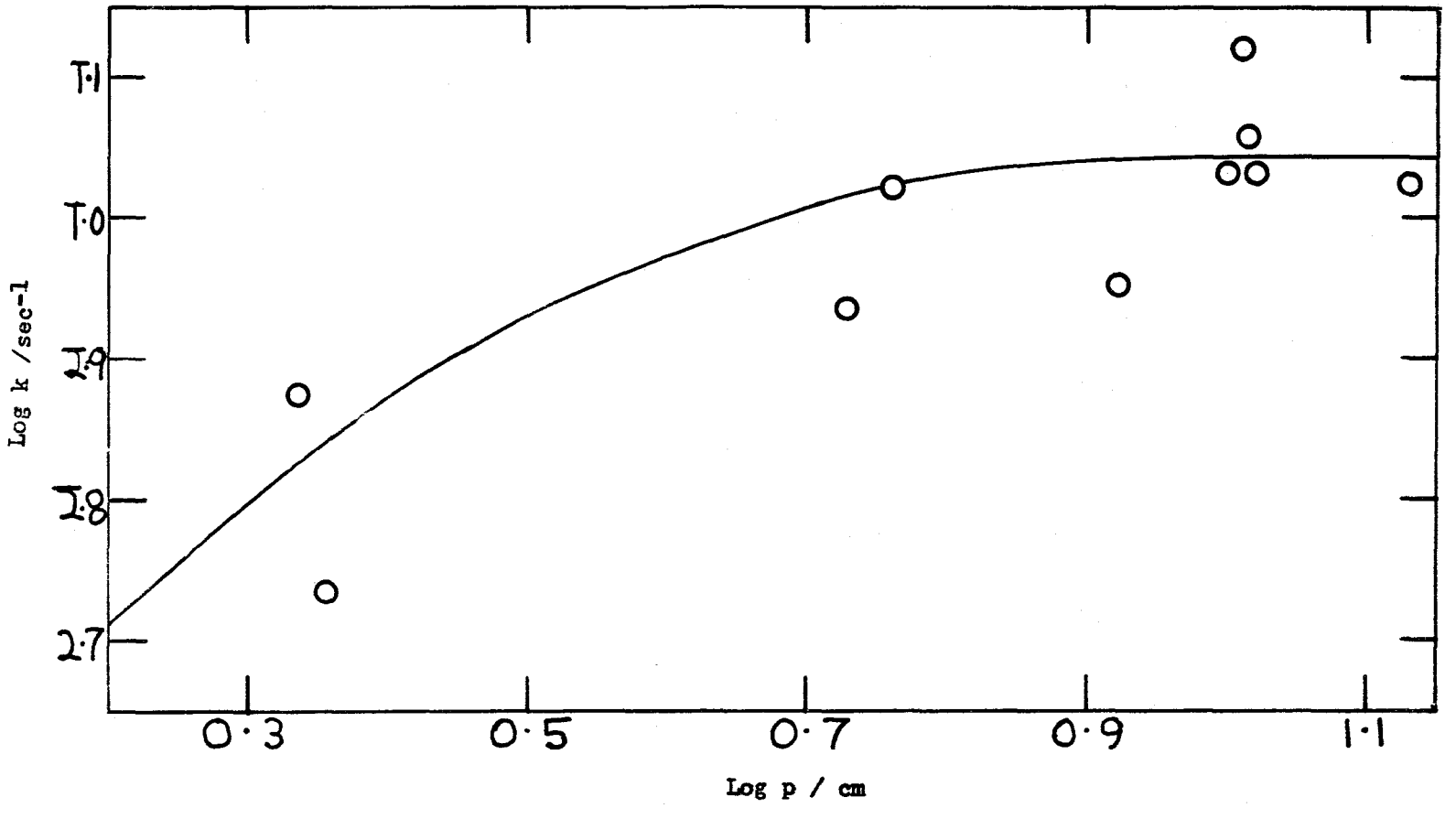


Fig. 17: The Variation Of The Rate Constant With Pressure For Cadmium Dimethyl
T = 744°K

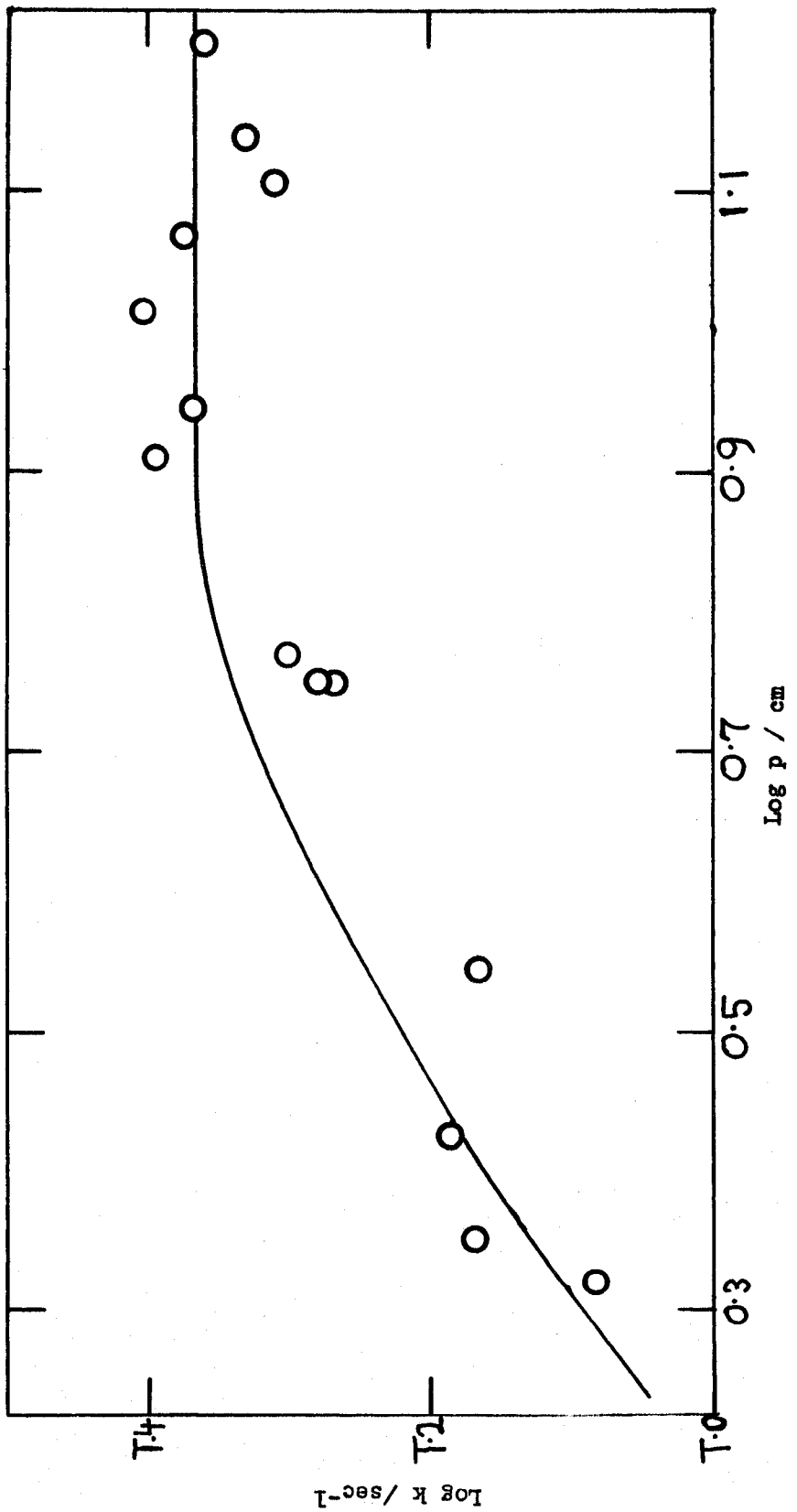


Fig. 18: The Variation Of The Rate Constant With Pressure For Cadmium Dimethyl T = 761°K

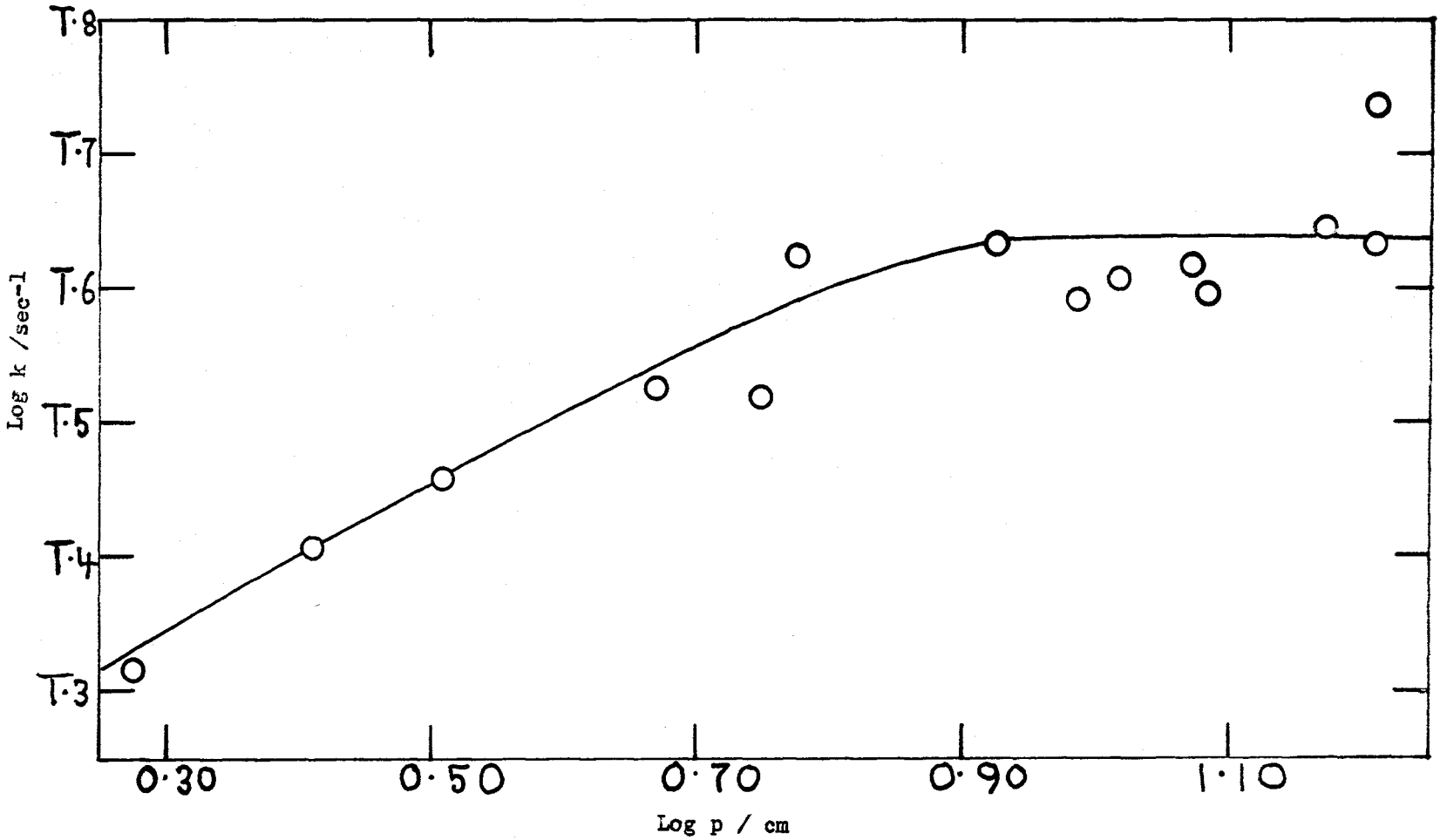


Fig. 19: The Variation Of The Rate Constant With Pressure For Cadmium Dimethyl T = 777°K

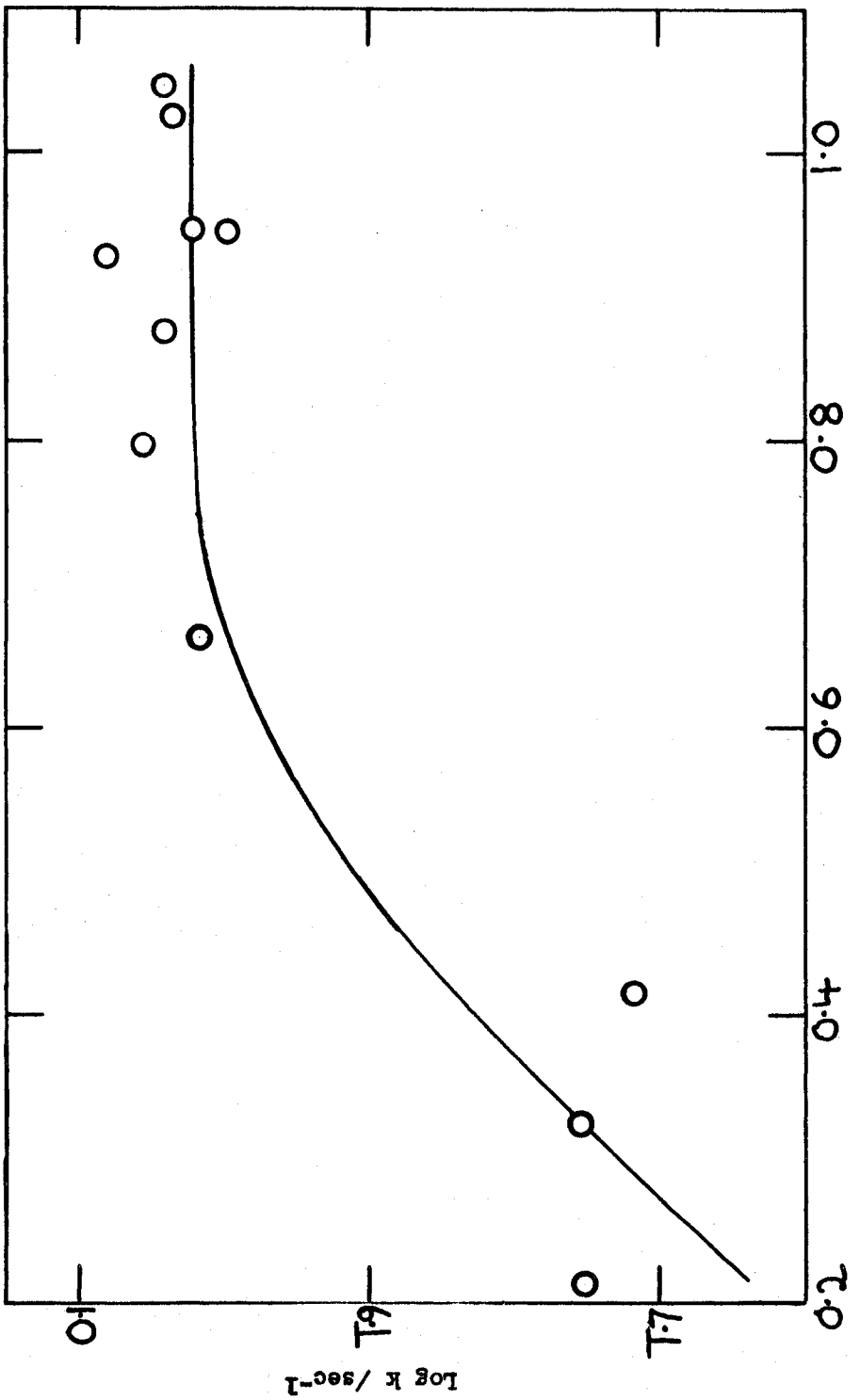


Fig. 20: The Variation Of The Rate Constant With Pressure For Cadmium Dimethyl T = 799°K

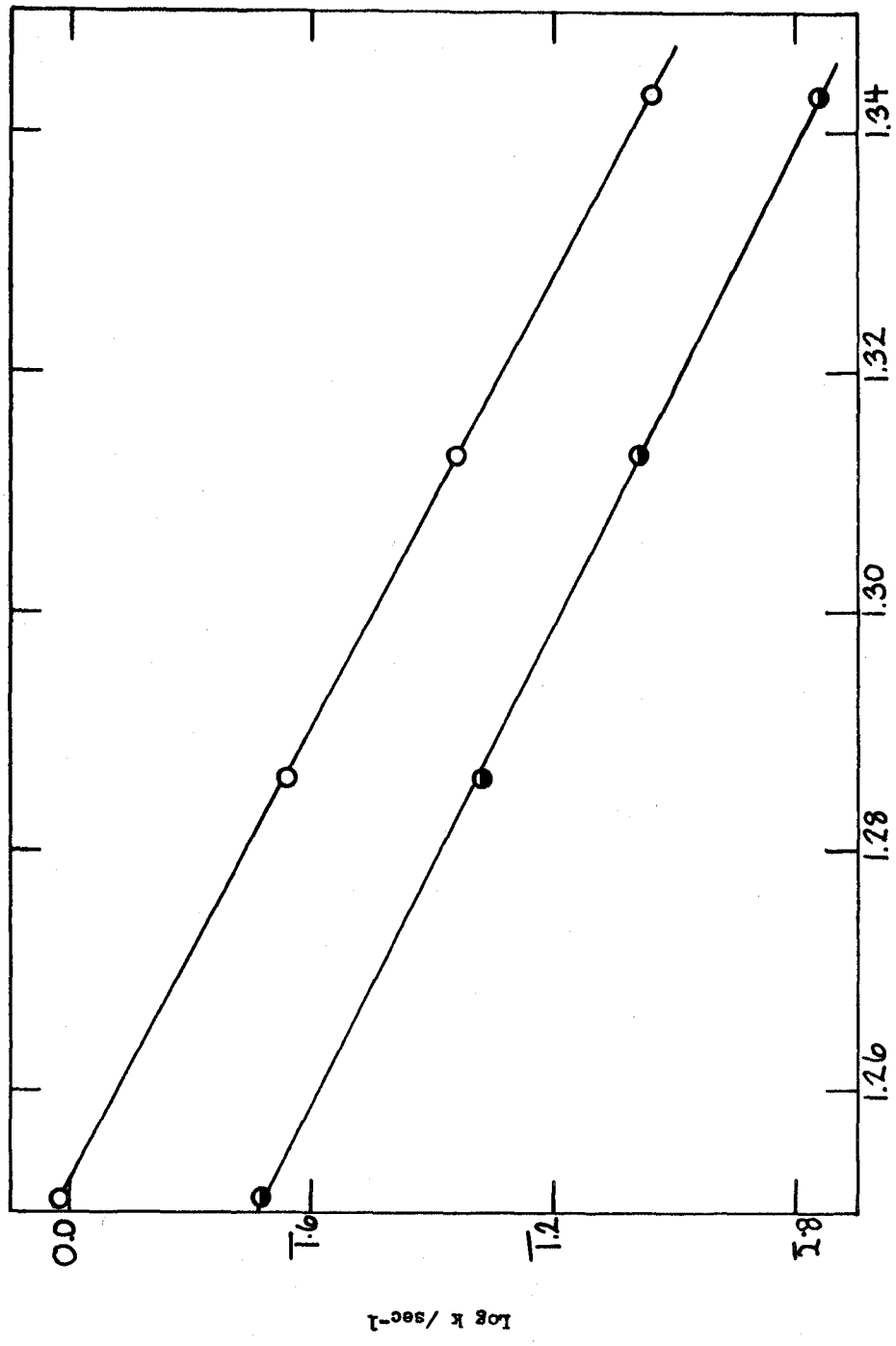


Fig. 21: Arrhenius Plots For The Decomposition Of Cadmium Dimethyl At The High Pressure Limit (○), And At 18 mm Pressure (●).

the original white solid readily melted at temperatures below 150°C. Preliminary infrared analyses indicated the presence of a mono-substituted phenyl derivative. The solid formed after exposure to air was dissolved in hydrochloric acid and titrated with 0.05 molar E.D.T.A. This analysis showed the solid contained 59.62% zinc by weight. This solid formation was not mentioned in previous work (1). However, much further work must be done on this compound and all the above discussion must presently be held as only tentative.

The Reaction of Methyl Radicals with Benzene

In the present work methyl radicals were produced by the thermal decomposition of the Group IIB methyl metallic alkyls. Stable molecules were formed from these radicals by the reactions,

$$CH_3 + C_6H_6 \longrightarrow CH_4 + C_6H_5 \qquad [a]$$

$$2CH_3 \longrightarrow C_2H_6 \,. \qquad [r]$$

If the assumption is made that the radicals were produced uniformly over the reaction zone and at a constant rate, then it can be seen that

$$\frac{d[CH_4]}{dt} = R[CH_4] = k_a[CH_3][C_6H_6]$$

$$\frac{d[C_2H_6]}{dt} = R[C_2H_6] = k_r[CH_3]^2 .$$

Therefore,

$$[CH_3] = \frac{R[CH_4]}{k_a[C_6H_6]} = \frac{(R[C_2H_6])^{\frac{1}{2}}}{(k_r)^{\frac{1}{2}}}$$

or,

$$\frac{k_a}{(k_r)^{\frac{1}{2}}} = \frac{R[CH_4]}{(R[C_2H_6])^{\frac{1}{2}}} \times \frac{1}{[C_6H_6]} .$$

The values of $k_a/(k_r)^{\frac{1}{2}}$ in Table 3 have been calculated from this expression. The rates of formation of the hydrocarbons were calculated from the total number of moles produced in a run. The expression used was

$$R[X] = \frac{(\text{total number of moles of X})}{(V)\ (t)} \text{ mole } cc^{-1} \text{ } sec^{-1}$$

where V is the volume of the reaction zone in cubic centimetres and t is the duration of the alkyl run in seconds. The concentration of benzene in moles cc^{-1} was calculated on the assumption that within the reaction zone benzene behaves as an ideal gas.

The value of $k_a/(k_r)^{\frac{1}{2}}$ at any temperature was found to be markedly dependent upon the total pressure in the system. This effect can be seen by reference to Figures 22, 23 and 24. These curves are representative curves of the ratio $k_a/(k_r)^{\frac{1}{2}}$ versus total pressure when the radical source was dimethyl mercury or dimethyl cadmium.

TABLE 3

Values of the Ratio $k_a/k_r^{\frac{1}{2}}$ from Different Alkyls

$k_a/k_r^{\frac{1}{2}}$ ($mole^{-\frac{1}{2}}$ $cc^{\frac{1}{2}}$ $sec^{-\frac{1}{2}}$)	Press. (cm)	Radical Source
111	11.12	dimethyl
66.0	10.60	cadmium
69.0	8.80	at 799°K
73.4	8.80	
52.4	8.48	
81.5	7.48	
78.3	6.28	
75.6	4.60	
69.7	2.61	
82.5	2.12	
93.1	1.63	
40.0	16.18	dimethyl
40.0	14.90	cadmium
50.6	13.20	at 777°K
45.9	12.10	
43.4	11.86	
45.7	10.42	
50.0	9.70	
56.9	8.44	
56.0	6.00	
53.1	5.60	
53.4	4.70	
54.2	3.23	
57.8	2.58	
69.2	1.88	
30.4	16.20	dimethyl
37.8	13.80	cadmium
36.9	13.76	at 761°K
34.2	12.74	
39.4	11.70	
41.2	10.36	
45.8	8.80	
40.5	8.12	
43.3	5.86	
43.2	5.74	
41.9	5.60	
43.9	3.50	
64.4	2.66	
56.1	2.24	
50.6	2.09	
28.9	13.46	dimethyl
35.6	10.50	cadmium
38.4	10.32	at 744°K
33.7	10.26	
34.6	10.04	
41.1	8.40	
41.0	5.76	
62.9	5.46	
37.6	5.36	
49.3	2.27	
44.9	2.16	
52.3	21.8	dimethyl
52.2	15.4	mercury
50.7	13.0	at 800°K
73.2	4.0	
70.6	7.4	
36.4	26.0	dimethyl
40.7	18.6	mercury
73.5	10.6	at 784°K
63.7	8.0	
63.8	7.8	
72.4	2.9	
82.5	2.8	
81.6	2.3	
73.5	1.89	
111	1.10	
105	1.05	
37.8	13.44	dimethyl
43.2	12.36	mercury
		at 771°K
31.6	15.65	dimethyl
34.8	13.72	mercury
35.8	11.25	at 760°K
39.0	7.86	
45.2	5.02	
51.8	2.71	
61.4	1.02	
189.9	0.36	
36.5	10.0	dimethyl
39.0	9.90	mercury
38.2	9.60	at 753°K
29.8	11.40	dimethyl
33.4	10.70	mercury
		at 744°K
19.35	10.6	dimethyl
19.71	10.4	mercury
20.78	10.3	at 724°K
21.2	9.8	
22.8	9.4	
17.66	12.74	dimethyl
19.99	10.0	mercury
20.42	7.9	at 720°K
20.28	5.4	
21.5	2.48	
89.6	0.41	
11.97	12.20	dimethyl
25.8	17.8	mercury
37.9	11.8	at 706°K
13.4	11.4	
7.26	14.26	dimethyl
9.59	7.5	mercury
19.36	2.65	at 695°K
21.6	2.00	
19.3	0.75	
12.52	9.46	dimethyl
11.3	9.12	mercury
11.9	8.80	at 693°K

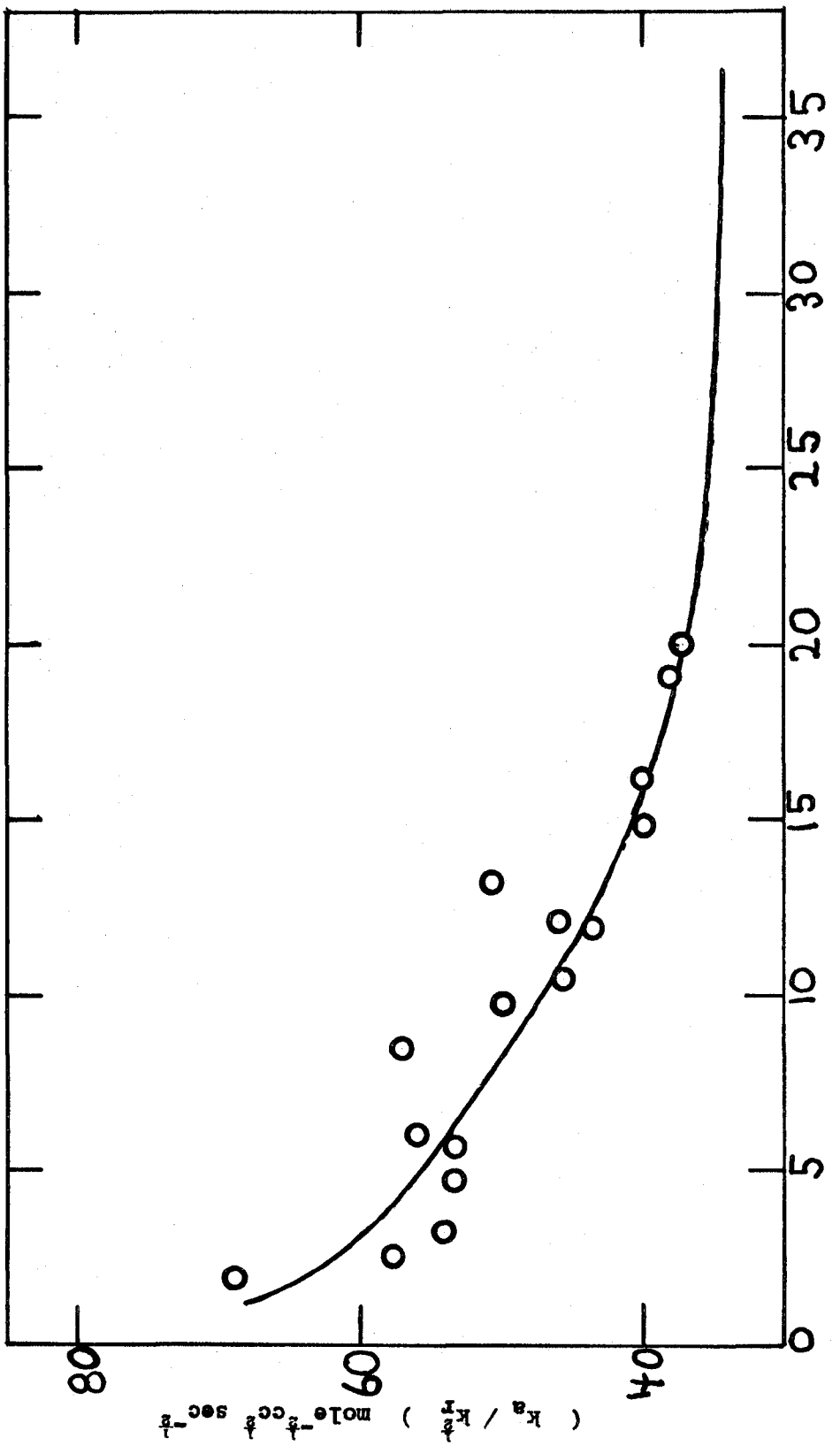


Fig. 22. The Variation of ($k_a / k_r^{\frac{1}{2}}$) With Pressure.
Source: $Cd(CH_3)_2$. T = 777°K.

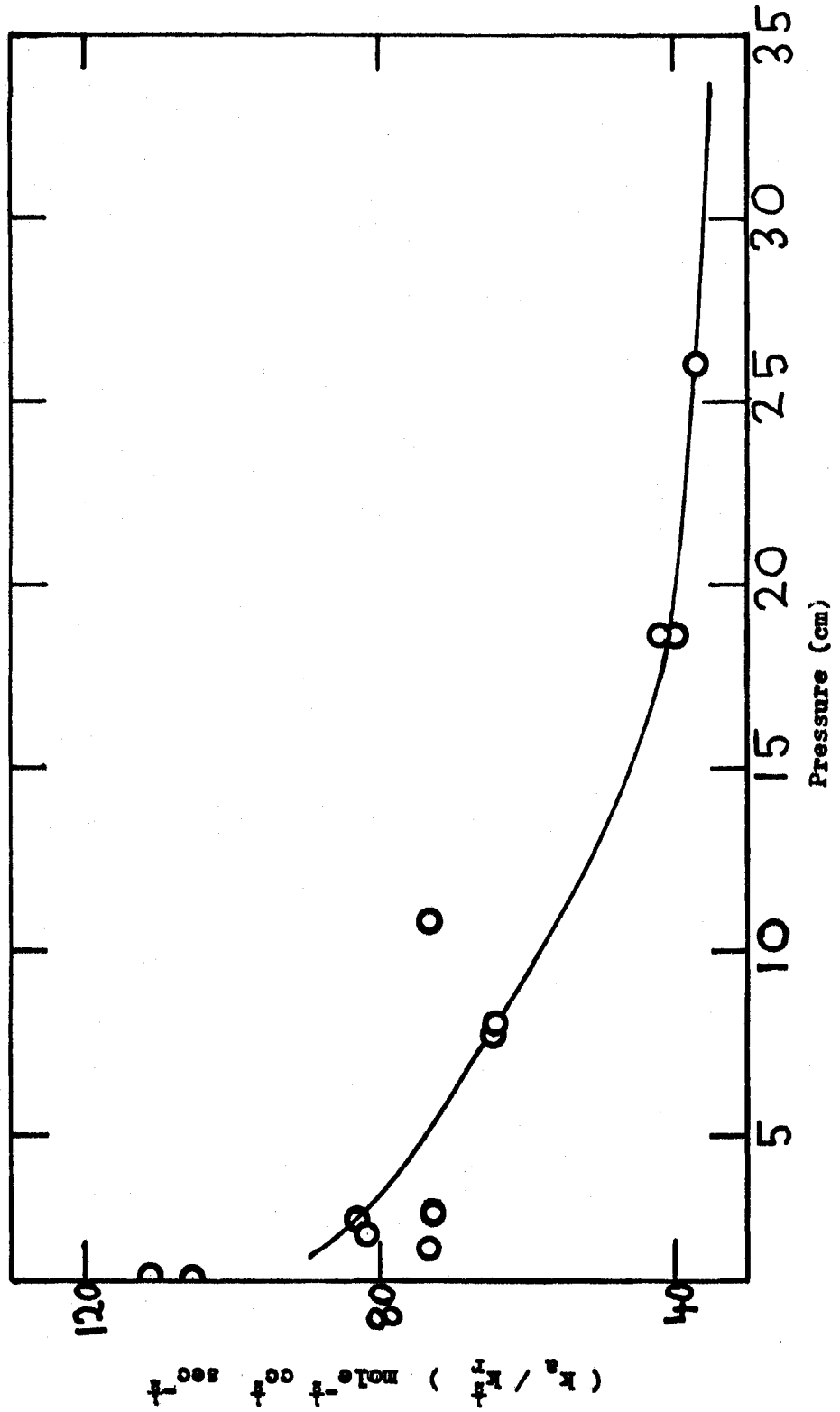


Fig. 23: The Variation of ($k_a / k_r^{\frac{1}{2}}$) With Pressure.
Source: $Hg(CH_3)_2$. T = 784°K.

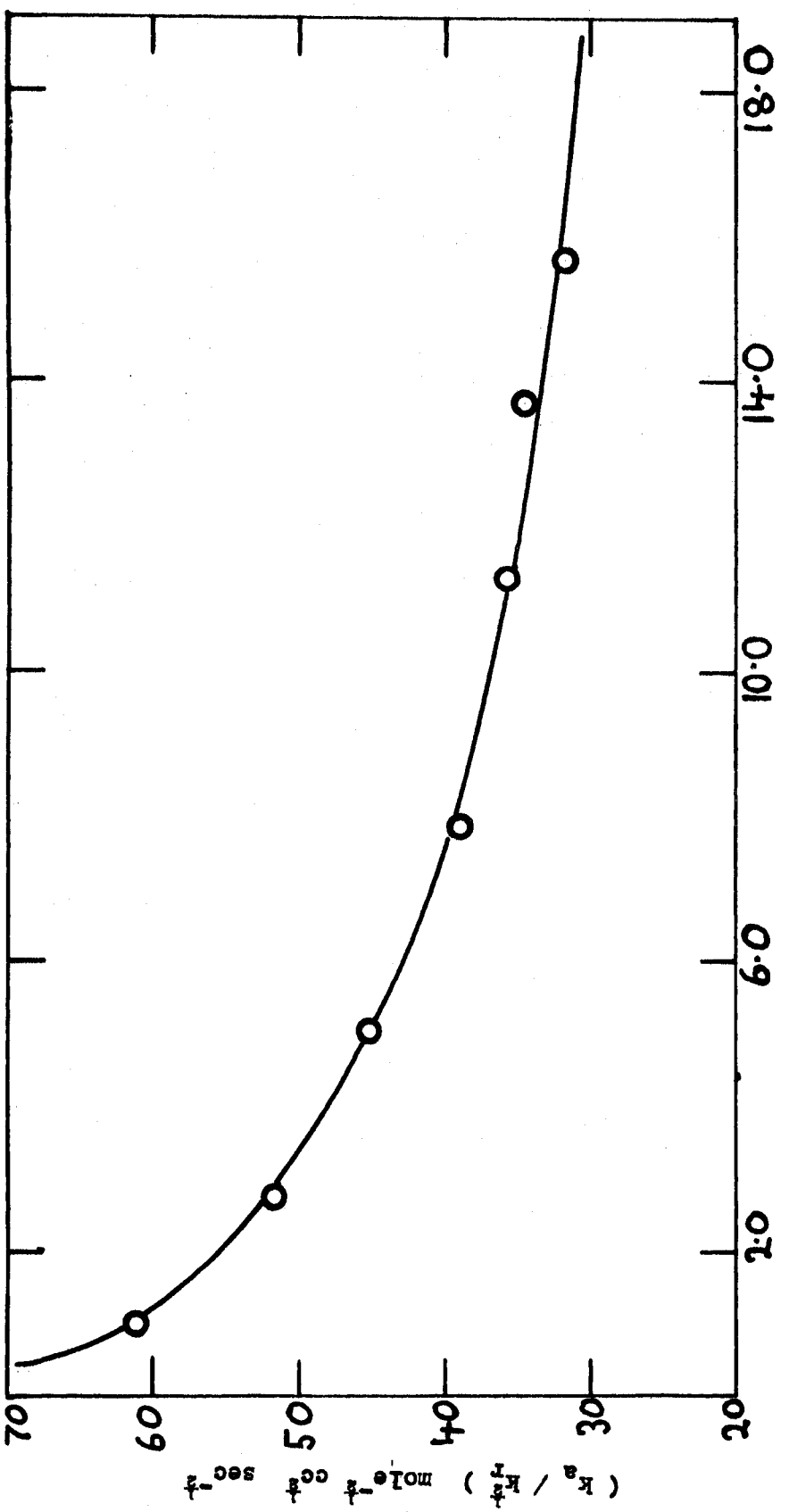


Fig. 24: The Variation of ($k_a / k_r^{\frac{1}{2}}$) With Pressure.
Source: $Hg(CH_3)_2$. T = 760°K.

Arrhenius plots of $k_a/(k_r)^{\frac{1}{2}}$ are given in Figure 25. These plots correspond to total pressures in the system of 2 centimetres, 6 centimetres, 12 centimetres and infinite pressure. The plot for infinity was made by using the best extrapolated values obtainable from the pressure curves. Since there is a large range for the extrapolated values, this range is shown graphically in Figure 25.

The plots in Figure 25 may be represented as follows:

at 2 cm:

$$\log (k_a/k_r^{\frac{1}{2}}) / \text{mole}^{-\frac{1}{2}}\ \text{cc}^{\frac{1}{2}}\ \text{sec}^{-\frac{1}{2}} = 6.3 - (15{,}600 / 2.303\ RT);$$

at 6 cm:

$$\log (k_a/k_r^{\frac{1}{2}}) / \text{mole}^{-\frac{1}{2}}\ \text{cc}^{\frac{1}{2}}\ \text{sec}^{-\frac{1}{2}} = 5.8 - (14{,}500 / 2.303\ RT);$$

at 12 cm:

$$\log (k_a/k_r^{\frac{1}{2}}) / \text{mole}^{-\frac{1}{2}}\ \text{cc}^{\frac{1}{2}}\ \text{sec}^{-\frac{1}{2}} = 5.4 - (13{,}300 / 2.303\ RT);$$

at infinite pressure:

$$\log (k_a/k_r^{\frac{1}{2}}) / \text{mole}^{-\frac{1}{2}}\ \text{cc}^{\frac{1}{2}}\ \text{sec}^{-\frac{1}{2}} = 4.4 - (10{,}500 / 2.303\ RT).$$

Using the value of Shepp (5) for $\log A_r$, 13.4 cc mole^{-1} sec^{-1}, and assuming $E_r = 0$ gives $\log k_a = 11.1 - (10{,}500/2.303\ RT)$.

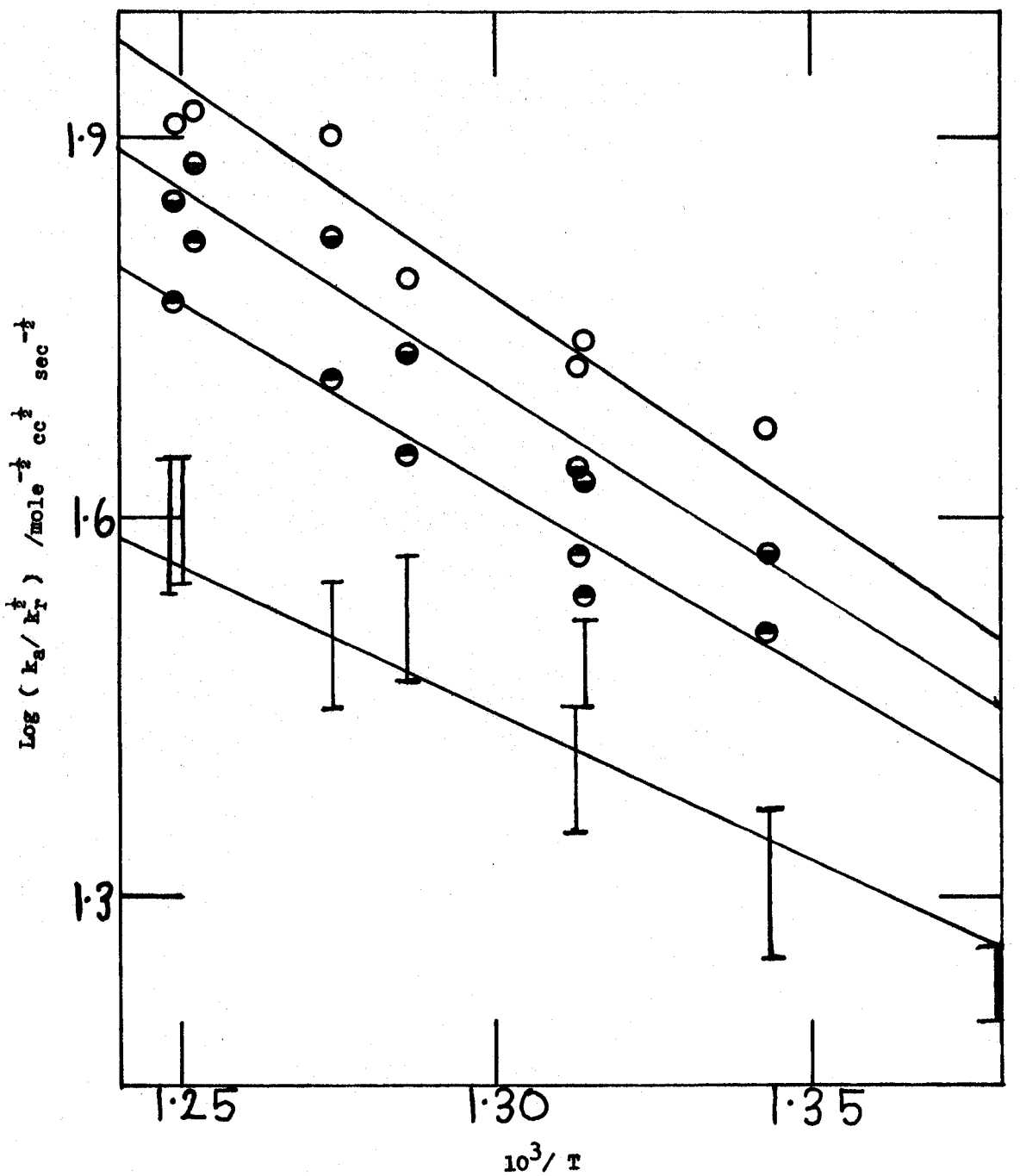


Fig. 25: Arrhenius Plots Of Log ($k_a / k_r^{\frac{1}{2}}$) Against 10^3/ T For Different Pressures.
- 2 cm Pressure
- 6 cm Pressure
- 12 cm Pressure
- Infinite Pressure

CHAPTER IV

DISCUSSION

Cadmium Dimethyl

As was previously stated, the mean bond energy, or the overall bond dissociation energy, can be determined by thermochemical means, if all the required information is available. In general,

$$D(CH_3 - X - CH_3) = \Delta H_f^\circ(X) + 2\,\Delta H_f^\circ(CH_3) - \Delta H_f^\circ(CH_3 - X - CH_3).$$

The following information is available for the cadmium case. $D(CH_3 - H) = 102.5$ kcal mole^{-1} (30), $\Delta H_f^\circ(H) = 52.089$ kcal mole^{-1} (31), $\Delta H_f^\circ(CH_4) = -17.889$ kcal mole^{-1} (31). From the above, it follows that $\Delta H_f^\circ(CH_3) = 32.5$ kcal mole^{-1}. Also, $\Delta H_f^\circ(CH_3 - Cd - CH_3 \text{gas}) = 26.4$ kcal mole^{-1} (32), and the heat of atomization of cadmium is 27.0 ± 0.2 kcal mole^{-1} (32). From this information,

$$\begin{aligned} D(CH_3 - Cd - CH_3) &= 27.0 + 2(32.5) - 26.4 \\ &= 65.6 \text{ kcal mole}^{-1}. \end{aligned}$$

The experimental activation energy determined in the present research was 48.8 kcal mole^{-1}, which is associated with $D(CH_3 - Cd\cdots CH_3)$, that is, the initial split of the metal-methyl bond. Using this value and the previously

derived value from thermochemistry for the two methyl-cadmium bonds gives

$$D(CH_3 - Cd\cdots CH_3) = 48.8 \text{ kcal mole}^{-1}$$

and

$$D(CH_3\cdots Cd) = 16.8 \text{ kcal mole}^{-1}.$$

The present results compare favourably with that of previous workers (2,25).

The results obtained by Price and Trotman-Dickenson (2) for the pyrolysis of dimethyl cadmium using a toluene carrier at 18 mm, and the present results using a benzene carrier at 18 mm, agree within the limits of uncertainty placed on the values.

The activation energy obtained by Laurie and Long (25) was reported as 43.5 ± 1.4 kcal mole^{-1} based on an assumed frequency factor of 1.2×10^{13}. This value of the frequency factor was chosen because of previous work on dimethyl mercury (28) and the results of Price and Trotman-Dickenson (2). This work was carried out at sufficiently high pressures at the low temperature studied, 531°K, that the activation energy should be close to the high pressure limit. A comparison of results was made by using the frequency factor determined in the present reseach in their equation and thus determining a value of E. This value for E is still

$$\overline{5}.155 = 13.4 - (E / 2.303 \times 1.987 \times 531)$$

or

$$E = 44.2 \text{ kcal mole}^{-1}$$

lower than the value determined in the present work, but this is not too surprising, considering the fact that Laurie and Long studied this reaction only at one temperature and they used a static system where the surface effect was quite pronounced and where side reactions could easily lead to low results.

Mercury Dimethyl

The thermochemical data necessary for the evaluation of the mean bond energy for mercury dimethyl is given below.

$$\Delta H_f^\circ(Hg(CH_3)_2 gas) = 20.78 \text{ kcal mole}^{-1} \quad (32)$$

$$\Delta H_f^\circ(Hg(g)) = 14.71 \text{ kcal mole}^{-1} \quad (32)$$

From this data and from $\Delta H_f^\circ(CH_3)$ as previously outlined $D_1(CH_3 - Hg\cdots CH_3) + D_2(CH_3\cdots Hg)$ was evaluated as 58.9 kcal mole^{-1}. The present results give the energy of activation E_1 to be 53.7 kcal mole^{-1} so that $D_1(CH_3\cdots Hg)$ should be assigned a value of 5.2 kcal mole^{-1}.

In the reaction scheme evolved for the decomposition of mercury dimethyl, the removal of methyl radicals by reaction [6] was considered to be very minor. This conclusion was arrived at through the following theoretical considerations. Methyl radicals may be removed from the system by the following reactions:

$$2CH_3 \longrightarrow C_2H_6 \qquad [4]$$

$$CH_3 + C_6H_6 \longrightarrow CH_4 + C_6H_5 \qquad [3]$$

$$CH_3 + C_6H_5 \longrightarrow C_6H_5CH_3 \qquad [6].$$

By use of the collision theory calculations for frequency factors, it can be shown that $A_4 \simeq 2A_6$. Reaction [4] is a simple radical recombination reaction and is assumed to have zero activation energy. Reaction [6] is also a radical recombination reaction, but the size effect of the phenyl radical is such that the energy of activation has been assigned a value of 2 kcal $mole^{-1}$. Therefore,

$$k_4 = 2A_6 \; e^{-0/RT}$$

and

$$k_6 = A_6 \; e^{-2000/RT}.$$

If a ratio of k_4/k_6 is taken, the following expression is obtained.

$$\frac{k_4}{k_6} = \frac{2}{.25} = 8$$

From simple collision theory considerations, reaction [6] will have approximately 1/8 the rate constant of reaction [4].

Suppose Figure 26 is considered as a qualitative picture of what actually occurs in a reaction zone. Most of the methyl radicals are released at the inlet of the reaction zone, and in the first few volume units of the zone, the methyl radicals are therefore at the highest concentration. For production of phenyl radicals, reaction [3] must

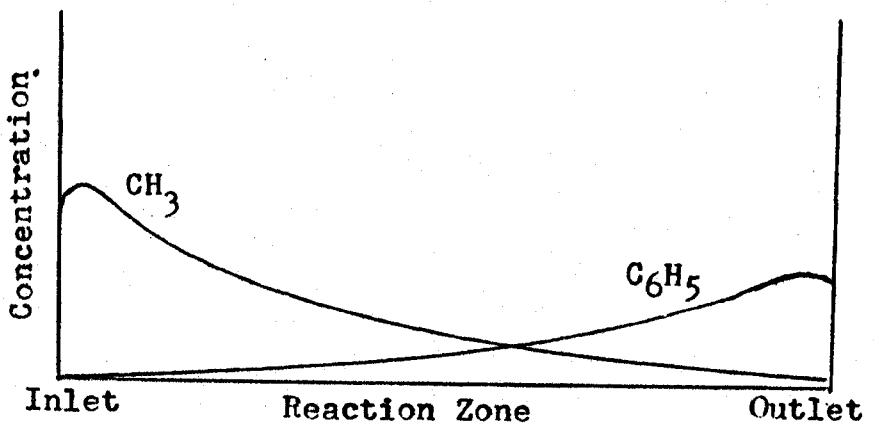


Fig. 26: Schematic Diagram For The Radical Concentrations In The Reaction Zone

first occur so that the net effect is that the concentration of phenyl radicals along the reaction zone is highest near the outlet. The relative average rate of reaction [4] will therefore be substantially greater than that of reaction [6].

When the dimethyl cadmium was studied, the above postulate was tested experimentally and even when the ratio of benzene to alkyl was low and reaction [6] might be expected to have some effect, the maximum removal of methyl radicals via reaction [6] was 5%. Dimethyl mercury is a considerably "cleaner" compound than is the dimethyl cadmium and any

side reactions should have less effect in the case of dimethyl mercury.

It was mentioned previously that many studies have been carried out on the pyrolysis of mercury dimethyl. However, the work done by Russel and Bernstein (29) has cast doubt on all previous static system measurements. The previous results were questioned because of the complexities arising via side reactions during the pyrolysis. The effect of the complicating side reactions was to obscure the actual mechanism of the decomposition. In the work of Russel and Bernstein it was observed that if an inhibitor such as cyclopropane was added to the system, the mechanism of the inhibited reaction was much less complex and the use of a steady state treatment of the results allowed a postulate of the mechanism for the inhibited decomposition to be made.

The work of Russel and Bernstein has recently been questioned by Cattanach and Long (33). These workers report that Russel and Bernstein assumed a low stability for the radical CH_2HgCH_3 and obtained in the experiments with added inhibitor, an extrapolated frequency factor for the reaction $Hg(CH_3)_2 \longrightarrow HgCH_3 + CH_3$ in the high pressure region which was almost certainly too high. The high value obtained was a result of ignoring the hydrogen produced in considerable quantities in the presence of cyclopropane. Hydrogen had previously been shown by other investigators (3,26) to have a profound effect on the alkyl decomposition. According

to the work of Gowenlock, Polanyi and Warhurst (3) in their flow system study of the pyrolysis of dimethyl mercury, the value of the rate constant was increased by a factor of four when hydrogen was used as a carrier gas. The postulated reaction of hydrogen with the alkyl was $H + Hg(CH_3)_2 \longrightarrow CH_4 + HgCH_3$. For all other carrier gases used, such as carbon dioxide or carbon dioxide and added toluene, there was no apparent reaction of the carrier with the parent compound as occurred in the foregoing case. Based on these observations and also on the work of Cunningham and Taylor (26) who also noted a hydrogen effect, Cattanach and Long have reported that the activation energy and the frequency factor determined by Russel and Bernstein were misleading, and the conclusion that $HgCH_3$ was thermally unstable and proceeded to dissociate with zero energy of activation was invalid.

Another static system pyrolysis of dimethyl mercury by Kallend and Purnell (34) has recently been published. Initially, these workers studied the heterogeneous part of the alkyl decomposition in an attempt to check previous static system data to see whether the discrepancy in the results was due to a surface effect. It was reported that washing the reaction vessels prior to use with nitric or chromic acid, surface coating with KCl or carbon coating by an overnight pyrolysis with propylene pre-conditioned the vessel surface such that no heterogeneous contribution could

be detected. If the vessel was washed with distilled water only, an increased surface effect was reported.

The second part of the research by these workers was on the homogeneous pyrolysis of the alkyl, both alone and in the presence of added gases. In the case of the reaction inhibited with excess propylene, E was determined to be 57.6 kcal $mole^{-1}$ and log A = 15.7. This value of E was assigned to $D_1(CH_3 - Hg\cdots CH_3)$, and applying steady state calculations led these workers to the conclusion that the determined energy of activation should be numerically equal to the sum of D_1 and D_2 such that $D_2(CH_3\cdots Hg)$ should have a zero energy of activation.

From a study of the various static system investigations of mercury dimethyl, it became evident that the results obtained with an uninhibited system were questionable. The degree and complexity of side reactions is such that the true mechanism cannot be unambiguously ascertained. When the reaction is inhibited by addition of cyclopropane or propylene, however, the results are usually much more satisfactory. The only factor which could cast doubt on these inhibited results is the degree of inhibition. The maximum value of the inhibitor to alkyl ratio in a static system is governed by the size of the reaction vessel and the minimum concentration of products required for analysis. Flow system studies have shown that inhibitor to alkyl ratios as high as 200 may be required (35) to give full inhibition. To reach ratios

of this type in a static system would require either a reaction vessel of abnormal size or more precise analytical techniques than are normally employed.

It is possible that there was some small surface effect in the present work, although the reaction vessel was acid-washed prior to use (34). Any small surface effect would cause the value of the activation energy obtained to be lower than the true value.

Finally, the assumption by Russel and Bernstein (29) and by Kallend and Purnell (34) that $D_2(CH_3 \cdots Hg)$ proceeds with zero activation energy must be questioned not only on the basis of the inhibition and the work of Cattanach and Long but also because the latest thermochemical data places $D_1(CH_3 - Hg \cdots CH_3) + D_2(CH_3 \cdots Hg)$ at a value of 58.9 kcal $mole^{-1}$ (32), so that even if the static system value is accurate, $D_2(CH_3 \cdots Hg)$ still will have an activation energy of 1.3 kcal $mole^{-1}$.

The present results are in very good agreement with previous flow system data, if the lower pressure work is considered. Table 4 shows, in summary form, dimethyl mercury pyrolysis data from both static and flow systems. Work carried out in uninhibited systems has been omitted.

Tests of Unimolecular Theory

As was previously stated, Slater (11,12) has postulated that if the unimolecular rate constant is measured in a

TABLE 4

Summary of Mercury Dimethyl Pyrolysis Data

Pressure (mm)	Temp. Range (^{o}C)	E kcal mole^{-1}	Log A	k^{*} (sec^{-1})	Method	Reference
10	489-552	51.5 ± 2	13.5	5.6×10^{-4}	Flow CO_2 + 3 mm toluene	3
16	465-608	50.1 ± 1.0	13.1	5.5×10^{-4}	Flow toluene	(1,2)
16	420-523	51.0 ± 1.0	13.6	1.0×10^{-3}	Flow benzene	‡
100	420-519	53.7 ± 1.0	14.8	2.0×10^{-3}	Flow benzene	‡
360	290-376	57.9 ± 1.4	15.7	6.8×10^{-4}	Static cyclopentane inhibited	29
500	375-436	57.6 ± 1.0	15.7	9.8×10^{-4}	Static propylene inhibited	34

k^{*} - calculated from A and E at 400^{o}C.

‡ - present work.

pressure independent region the relationship between the experimentally determined activation energy E and the activation energy at infinite pressure, E_∞, is expressed by the relation

$$E = E_\infty - \tfrac{1}{2}n' RT\, g(\theta).$$

When the experimental curves of log k/k_∞ versus log P from the present work were compared with standard curves obtained by Slater (12), agreement was obtained when the effective number of oscillators, n', was taken as 13 for both $Cd(Me)_2$ and $Hg(Me)_2$.

Previous work by Price and Trotman-Dickenson (2) was carried out in a region of pressure dependence. Their results for the cadmium and mercury dialkyls were very close to the present values determined at the same pressures. Using their results and the knowledge that the number of effective oscillators was in the region $n' = 13$, the previous activation energies were corrected to a region of pressure independence.

It was found in the case of cadmium dimethyl from a comparison of the plot log k/k_∞ versus log P that the slope corresponding to $n' = 13$ best fitted the curve at a value of log $k/k_\infty = -1.28$ ($k/k_\infty = .05$). The closest value obtainable for $g(\theta)$ from Table 5 was .45, which was an approximation made by interpolation of the available data. At a temperature of 770°K, the mid-temperature used in the current research, this gave

TABLE 5

Values of Pressure Dependent Parameter θ

θ	$\frac{k}{k_\infty}$	g(θ) (n' = 15)	g(θ) (n' = 9)
10^8	0.923	---	---
10^7	0.737	0.150	---
10^6	0.448	0.285	---
10^5	0.197	0.428	0.013
10^4	0.063	0.556	0.081
10^3	0.0155	0.663	0.245
10^2	0.0030	0.747	0.452

$$E_\infty = (45.8 \pm 1) + \tfrac{1}{2} \times 13 \times 1.987 \times 770 \times .45$$

$$= 50.3 \pm 1 \text{ kcal mole}^{-1}.$$

The limits of error placed on this result were based solely on the stated limits of the experimental work of Price and Trotman-Dickenson (2) and should be assumed to be a minimum value.

When the same curve-fitting was made for mercury dimethyl, a value of $k/k_\infty = .199$ was obtained. The closest value for $g(\theta)$ from Table 5 was .40. At a central temperature of 750°K, this gave

$$E_\infty = (50.1 \pm 1) + \tfrac{1}{2} \times 13 \times 1.987 \times 750 \times .40$$

$$= 54.0 \pm 1 \text{ kcal mole}^{-1}.$$

In the mercury case, the agreement between the predicted value, 54 ± 1 kcal mole^{-1}, and the present experimental value of 53.7 ± 1 kcal mole^{-1} was excellent. The extent of agreement in the cadmium dimethyl case, 50.3 ± 1 kcal mole^{-1} from the low pressure results and Slater's theory, versus 48.8 ± 1 kcal mole^{-1} observed experimentally was not as satisfactory although it was within the limits of experimental error. A portion of the difference, approximately .6 kcal mole^{-1}, may be due to an over-estimation of the effect of pressure on the rate constant resulting from loss of methyl radicals by competing side reactions.

The overall agreement obtained may be taken as a good indication that Slater's theory may be applied successfully to these compounds.

The Reaction of Methyl Radicals with Benzene

The values of $k_a/k_r^{\frac{1}{2}}$ have been calculated using the equation

$$\frac{k_a}{k_r^{\frac{1}{2}}} = \frac{\text{moles } CH_4}{(\text{moles } C_2H_6)^{\frac{1}{2}}} \times \frac{T}{P} \times 2.75 ,$$

where the value 2.75 incorporates all the constants for a five minute alkyl run.

In the derivation of this equation it has been assumed that methyl radicals are uniformly released over the entire reaction zone and that the production of radicals occurs at a constant rate. The production of radicals at a constant rate can be realized experimentally, since the alkyl reservoir temperature can be kept constant thus supplying a constant alkyl feed throughout the course of a run. However, the uniform release of methyl radicals throughout the reaction zone can never be obtained although this condition will be approached when the percentage decomposition is small. At higher percentage decomposition a large portion of the methyl radicals will be released in a comparitively small section of the overall reaction volume. This non-uniform release has two effects on the ratio of $k_a/k_r^{\frac{1}{2}}$. Initially, the concentration of methyl radicals at the beginning of the reaction zone will be so high that the rate of the recombination reaction will be greatly enhanced. As the carrier flow proceeds along the length of the reaction

zone the methyl concentration will decrease and the abstraction reaction will occur preferentially. These two effects are somewhat self-compensating. The net overall result is that there is no marked experimental effect (1).

One further effect must be considered. Inherent in the equation for $k_a/k_r^{\frac{1}{2}}$ is the assumption that when two CH_3 radicals recombine the vibrationally excited C_2H_6 formed is stablized by collision and does not redissociate. In fact, under the experimental conditions used some redissociation will occur. The extent of this redissociation will be controlled by two factors. As the pressure in the system is increased a shorter average time will elapse between the formation of $C_2H_6^*$ and its deactivation by collision. Therefore the extent of redissociation will decrease as the pressure increases and in fact should approach zero as the pressure approaches infinity.

Secondly, as the temperature is increased the average thermal energy of the methyl radicals will be increased so that the $C_2H_6^*$ formed will have a shorter life. Therefore, at a fixed total pressure, the extent of redissociation will increase as the temperature is increased.

The net effect of these two factors should be to give the recombination process an apparent negative activation energy that will increase in magnitude as the pressure is decreased. This will lead to steeper Arrhenius curves of $k_a/k_r^{\frac{1}{2}}$ as the pressure is decreased.

The experimental results for the ratio of $k_a/k_r^{\frac{1}{2}}$ were given in Table 3 and Figure 25. The progression of values for the activation energy of the abstraction reaction from 2 centimetres to infinite pressure shows the general trend as discussed above. The true activation energy for the abstraction reaction should therefore be that observed for the extrapolated results at infinite pressure (10.5 kcal $mole^{-1}$). There was a great deal of scatter in the experimental results of $k_a/k_r^{\frac{1}{2}}$. The scatter is such that only trends can be ascertained, and the actual value quoted for E_a at infinite pressure should be considered as only a tentative value.

Summary

Most of the relevant information uncovered has been discussed and presented previously. However, for completeness, it is deemed necessary to point out that benzene used in a carrier system has certain definite advantages and some disadvantages.

For studies in the region of pressure independence benzene appears to be a much more efficient energy transfer agent. From previous work with a toluene carrier (1,2), it was assumed that a pressure of about 25-30 cm would be necessary to reach a pressure independent region. In the present work, the value of the rate constant was pressure independent above about 10 cm.

The main disadvantage of benzene is that it is a poorer radical scavenger than toluene, and the energy of activation for abstraction of a hydrogen from benzene might be very close to the energy of activation for abstraction from the parent alkyl. The alkyl radicals produced by reaction [A] may react at a different rate than the parent

$$R\bullet + CH_3 - M - CH_3 \longrightarrow RH + \bullet CH_2 - M - CH_3 \qquad [A]$$

alkyl and will give a different product distribution. This may be a major cause for the scatter in the present results, particularly at low pressures.

SUGGESTIONS FOR FURTHER RESEARCH

Investigations on mercury dimethyl should be carried out to see whether there is any appreciable surface effect. Also, some runs at very high benzene pressures should be made to determine better values of $k_a/k_r^{\frac{1}{2}}$ so that the range in the extrapolated values can be reduced. Finally, a few experiments should be carried out to determine how much effect reaction [6] has on the overall reaction.

If possible, a carrier gas consisting of a mixture of benzene in toluene should be used to make full use of the energy transfer properties of benzene and the radical scavenging properties of toluene. The probable best procedure would be to inject toluene into the benzene stream in a manner similar to that in which the alkyl was injected in the present work.

Finally, it might be profitable to study the Group IIB alkyls at very low pressures and long run times to see where the second order region occurs. This would have the dual purpose of checking the theory of unimolecular reactions and of determining just how low a ratio of carrier to alkyl can be used to give meaningful results and yet not use prohibitively long run times to get measureable amounts of products.

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